Pesticidally active ketone and oxime derivatives

The present invention relates (1) to compounds of formula

wherein

 A_0 , A_1 and A_2 are each independently of the others a bond or a C_1 - C_6 alkylene bridge which is unsubstituted or substituted by from one to six identical or different substituents selected from halogen and C_3 - C_6 cycloalkyl;

 A_3 is a C_1 - C_6 alkylene bridge which is unsubstituted or substituted by from one to six identical or different substituents selected from halogen and C_3 - C_6 cycloalkyl;

Y is O, NR_{11} , S, SO or SO_2 ;

M is O or NORs

X₁ and X₂ are each independently of the other fluorine, chlorine or bromine;

 R_1 , R_2 and R_3 are each independently of the others H, halogen, OH, SH, CN, nitro, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkylcarbonyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_1 - C_6 alkoxy, C_1 - C_6 alkoxy, C_2 - C_6 alkenyloxy, C_2 - C_6 alkenyloxy, C_2 - C_6 alkyl, C_1 - C_6 alkoxycarbonyl or C_3 - C_6 haloalkynyloxy; the substituents R_3 being independent of one another when m is 2;

Q is O, NR₁₁, S, SO or SO₂;

W is O, NR₁₁, S, SO, SO₂, -C(=O)-O-, -O-C(=O)-, -C(=O)-NR₁₁- or -NR₁₁-C(=O)-;

T is a bond, O, NR₁₁, S, SO, SO₂, -C(=O)-O-, -O-C(=O)-, -C(=O)-NR₁₁- or -NR₁₁-C(=O)-;

D is CH or N;

 R_4 is H, halogen, OH, SH, CN, nitro, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkylcarbonyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkenyloxy, C_2 - C_6 alkynyloxy, C_2 - C_6 alkyl, C_1 - C_6 -

alkoxycarbonyl, C_3 - C_6 haloalkynyloxy, NH_2 , $NH(C_1$ - C_6 alkyl) or $N(C_1$ - C_6 alkyl)₂ wherein the two alkyl groups are independent of one another; the substituents R_4 being independent of one another when k is greater than 1;

 R_5 is C_1 - C_{12} alkyl substituted by from one to five substituents selected from the group consisting of -N₃, NO₂, OH, C₃-C₈cycloalkyl, C₃-C₈cycloalkoxy, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₃-C₆alkynyloxy, C₃-C₆haloalkynyl, C₃-C₆haloalkynyl, C₃-C₆haloalkynyl-oxy, C₃-C₆cycloalkyl-C₁-C₆alkoxy, C₁-C₆alkylcarbonyl, C₁-C₆haloalkylcarbonyl, C₁-C₆alkoxy-C₁-C₆alkoxy, -P(=O)(OC₁-C₆alkyl)₂, -S(O)_q-R₁₃, NH₂, NH(C₁-C₆alkyl), N(C₁-C₆alkyl)₂ wherein the two alkyl groups are independent of one another, -N(R₇)₂ wherein the two R₇s are independent of one another and -NR₁₄S(O)qR₁₅;

 C_3 - C_8 cycloalkyl substituted by from one to five identical or different substituents selected from the group consisting of C_1 - C_6 alkyl, halogen, CN, NO₂, OH, C_1 - C_6 alkoxy, C_1 - C_6 haloalkoxy, NH₂, NH(C_1 - C_6 alkyl) and N(C_1 - C_6 alkyl)₂ wherein the two alkyl groups are independent of one another;

 $-N(R_7)_2$ wherein the two R_7 s are independent of one another;

 $-C(=O)-O-R_8$; $-C(=O)-R_9$; $-C(=O)-NH-R_9$; $-C(=N-O-R_9)R_{10}$; $-C(=N-NH-R_9)R_{10}$

-NR₁₄S(O)qR₁₅

wherein the alkenyl and alkynyl radicals are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five identical or different substituents selected from the group consisting of halogen, -N₃, CN, NO₂, OH, C₃-C₆cycloalkyl, C₁-C₆-alkoxy, C₁-C₆haloalkoxy, C₂-C₆haloalkenyloxy, C₃-C₆alkynyloxy, C₃-C₆alkynyloxy, C₃-C₆haloalkenyloxy, C₃-C₆alkynyloxy, C₃-C₆haloalkynyloxy, C₁-C₆alkoxy, C₁-C₆alkylcarbonyl, C₁-C₆haloalkylcarbonyl, C₁-C₆alkylcarbonyl-C₁-C₆alkyl, C₁-C₆alkoxycarbonyl-C₁-C₆alkyl, C₂-C₆alkyl, C₃-C₆alkyl, C₁-C₆alkyl, C₂-C₆alkenyloxy-C₁-C₆alkyl, C₂-C₆alkyl, C₂-C₆alkyl, C₂-C₆alkyl, C₃-C₆alkyl, C₃-C₆alkyl, C₁-C₆alkyl, -P(=O)(OC₁-C₆-alkyl)₂, -S(O)_q-R₁₃, NH₂, NH(C₁-C₆alkyl) and N(C₁-C₆alkyl)₂, wherein the two alkyl groups are independent of one another;

and wherein the heterocyclyl radical mentioned under R_5 are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five substituents selected from halogen, CN, NO₂, OH, SH, C₁-C₆alkyl, C₁-C₆haloalkyl, C₂-C₆alkenyl, C₂-C₆-haloalkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkyl, C₁-C₆alkyl, C₁-C₆alkoxy,

 $C_1\text{-}C_6\text{haloalkoxy},\ C_2\text{-}C_6\text{alkenyloxy},\ C_2\text{-}C_6\text{haloalkenyloxy},\ C_3\text{-}C_6\text{alkynyloxy},\ C_3\text{-}C_6\text{haloalkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_1\text{-}C_6\text{alkylcarbonyl},\ C_2\text{-}C_6\text{alkylcarbonyl},\ C_3\text{-}C_6\text{alkynylthio},\ C_3\text{-}C_6\text{cycloalkyl-}C_1\text{-}C_6\text{alkylthio},\ C_3\text{-}C_6\text{haloalkylthio},\ C_3\text{-}C_6\text{alkyloalkylthio},\ C_1\text{-}C_6\text{alkyloalkoxy-}C_1\text{-}C_6\text{alkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkyloalkyloalkenyloxy-}C_1\text{-}C_6\text{alkyloalkyl$

or, when A_0 is a C_1 - C_6 alkylene bridge, R_5 is C_2 - C_6 alkylene bonded to one of the carbon atoms of A_0 ;

or, when R_4 and a group $-C(=NOR_6)R_5$ are in the ortho-position relative to one another, R_4 and R_5 together form a C_2 - C_6 alkylene bridge wherein one or two CH_2 groups each independently of the other may be replaced by O, NR_{12} , S or SO, and wherein the CH_2 groups are unsubstituted or mono- or di-substituted by halogen, OH, SH, CN, nitro, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy or C_1 - C_6 haloalkoxy;

R₆ is H, C₁-C₁₂alkyl, C₃-C₈cycloalkyl, C₁-C₆alkylcarbonyl, C₂-C₆alkenyl, C₂-C₆alkynyl, aryl, heterocyclyl or benzyl, wherein the alkyl, cycloalkyl, alkenyl and alkynyl radicals are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five identical or different substituents selected from the group consisting of halogen, -N₃, CN, NO₂, OH, SH, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₃-C₆haloalkynyloxy, C₃-C₆cycloalkyl-C₁-C₆alkoxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxy-carbonyl-C₁-C₆alkylcarbonyl, C₁-C₆alkylthio, C₂-C₆alkenylthio, C₃-C₆alkylthio, C₃-C₆cycloalkyl-C₁-C₆alkylthio, C₃-C₆haloalkynyl, C₂-C₆haloalkenylthio, C₁-C₆alkylthio, C₃-C₆cycloalkyl-C₁-C₆alkyl, C₁-C₆alkoxy-C₁-C₆alkyl, C₂-C₆alkenyloxy-C₁-C₆alkyl, C₂-C₆haloalkenyloxy-C₁-C₆alkyl, C₂-C₆haloalkoxy-C₁-C₆alkyl, C₂-C₆alkyl, NH₂, NH(C₁-C₆alkyl), N(C₁-C₆alkyl)₂ wherein the two alkyl groups are independent of one another, C₁-C₆alkylcarbonylamino, C₁-C₆alkyl-aminocarbonylamino, C₁-C₆alkoxycarbonylamino and C₁-C₆alkyl-aminocarbonylamino;

and the aryl, heterocyclyl and benzyl radicals are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five identical or different substituents selected from the group consisting of halogen, CN, NO₂, OH, SH, C₁-C₆alkyl, C₁-C₆haloalkyl,

 $C_2\text{-}C_6\text{alkenyl},\ C_2\text{-}C_6\text{haloalkenyl},\ C_3\text{-}C_6\text{alkynyl},\ C_3\text{-}C_8\text{cycloalkyl},\ C_3\text{-}C_8\text{cycloalkyl},\ C_3\text{-}C_6\text{alkenyloxy},\ C_2\text{-}C_6\text{alkenyloxy},\ C_2\text{-}C_6\text{alkenyloxy},\ C_3\text{-}C_6\text{alkynyloxy},\ C_3\text{-}C_6\text{alkynyloxy},\ C_3\text{-}C_6\text{alkynyloxy},\ C_3\text{-}C_6\text{alkynyloxy},\ C_3\text{-}C_6\text{alkyloarbonyl},\ C_1\text{-}C_6\text{alkyloarbonyl},\ C_1\text{-}C_6\text{alkyloarbonyl},\ C_1\text{-}C_6\text{alkyloarbonyl},\ C_1\text{-}C_6\text{alkyloarbonyl},\ C_1\text{-}C_6\text{alkyloarbonyl},\ C_1\text{-}C_6\text{alkyloarbonyl},\ C_2\text{-}C_6\text{alkyloarbonyl},\ C_3\text{-}C_6\text{cycloalkyl-}C_1\text{-}C_6\text{alkyloarbonyl},\ C_3\text{-}C_6\text{alkyloarbonyl},\ C_2\text{-}C_6\text{alkyloarbonyl},\ C_2\text{-}C_6\text{alkyloarbonyl},\ C_2\text{-}C_6\text{alkyloarbonyl},\ C_2\text{-}C_6\text{alkyloarbonyloxy-}C_1\text{-}C_6\text{alky$

 R_7 is H, C_1 - C_6 alkyl, C_1 - C_3 haloalkyl, C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkoxycarbonyl, C_3 - C_8 cycloalkyl, C_3 - C_8 cycloalkylcarbonyl or formyl;

R₈ is H, C₁-C₁₂alkyl substituted by from one to five identical or different substituents selected from halogen, -N₃, CN, NO₂, OH, C₁-C₆alkoxy, C₁-C₆alkylthio, NH₂, NH(C₁-C₆alkyl), N(C₁-C₆alkyl)₂ wherein the two alkyl groups are independent of one another and C₁-C₆alkylcarbonylamino; C₃-C₆cycloalkyl, C₁-C₆alkylcarbonyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₂-C₆haloalkynyl, aryl, heterocyclyl or benzyl, wherein the aryl, heterocyclyl and benzyl radicals are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five substituents selected from the group consisting of halogen, CN, NO₂, OH, C₁-C₆haloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₃-C₆haloalkynyloxy, C₃-C₆haloalkynyloxy, C₃-C₆haloalkynyloxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylthio, C₂-C₆alkenylthio, C₃-C₆alkylthio, C₃-C₆haloalkylthio, C₁-C₆alkylthio, C₃-C₆haloalkylthio, C₁-C₆alkylthio, C₁-C₆alkylthion, C₁-C₆alkylthio

 R_9 is H, C_1 - C_{12} alkyl unsubstituted or substituted by from one to five identical or different substituents selected from halogen, CN, NO₂, OH, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, NH₂, NH(C_1 - C_6 alkyl), N(C_1 - C_6 alkyl)₂ wherein the two alkyl groups are independent of one another and C_1 - C_6 alkylcarbonylamino; C_3 - C_6 cycloalkyl, C_1 - C_6 alkylcarbonyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkynyl, aryl, heterocyclyl or benzyl, wherein the aryl, heterocyclyl and benzyl radicals are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five substituents selected from the group consisting

of halogen, CN, NO₂, OH, C₁-C₆haloalkyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆haloalkoxy, C₂-C₆alkenyloxy, C₂-C₆haloalkenyloxy, C₃-C₆alkynyloxy, C₃-C₆haloalkynyloxy, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkylthio, C₂-C₆alkenylthio, C₃-C₆alkynylthio, C₁-C₆alkylthio, C₃-C₆alkynylthio, C₁-C₆alkylthio, C₃-C₆alkynyl, NH₂, NH(C₁-C₆alkyl), N(C₁-C₆alkyl)₂ wherein the two alkyl groups are independent of one another, C₁-C₆alkylcarbonylamino, C₁-C₆haloalkylcarbonylamino, C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkylcarbonylamino and C₁-C₆alkylaminocarbonylamino;

 R_{10} is H, C_1 - C_{12} alkyl unsubstituted or substituted by from one to five identical or different substituents selected from halogen, CN, NO₂, OH, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, NH₂, NH(C_1 - C_6 alkyl), N(C_1 - C_6 alkyl)₂ and C_1 - C_6 alkylcarbonylamino; C_3 - C_8 cycloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkenyl, aryl, heterocyclyl or benzyl, wherein the aryl, heterocyclyl and benzyl radicals are unsubstituted or, depending upon the possibilities of substitution, substituted by from one to five identical or different substituents selected from the group consisting of halogen, CN, NO₂, OH, SH, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_3 - C_8 cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 haloalkoxy, C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkylcarbonyl- C_1 - C_6 alkyl, C_1 - C_6 alkoxy- C_1 - C_6 alkyl, NH₂, NH(C_1 - C_6 alkyl), N(C_1 - C_6 alkyl) wherein the two alkyl groups are independent of one another, C_1 - C_6 alkylcarbonylamino, C_1 - C_6 alkoxycarbonylamino and C_1 - C_6 alkylaminocarbonylamino;

 R_{11} and R_{12} are each independently of the other H, C_1 - C_6 alkyl, C_1 - C_3 haloalkyl, C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkylcarbonyl, C_3 - C_8 cycloalkyl, C_3 - C_8 cycloalkyl- C_1 - C_6 alkyl or C_3 - C_8 cycloalkylcarbonyl; and

 R_{13} is H, C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_3 - C_6 alkynyl or C_1 - C_6 haloalkyl;

R₁₄ is H, C₁-C₆alkyl, C₂-C₆alkenyl, C₃-C₆alkynyl or C₁-C₆haloalkyl;

 R_{15} is H, C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_3 - C_6 alkynyl or C_1 - C_6 haloalkyl;

k is 0, 1, 2, 3 or 4;

m is 1 or 2; and

q is 0, 1 or 2;

and, where applicable, their possible E/Z isomers, E/Z isomeric mixtures and/or tautomers, in each case in free form or in salt form, to a process for the preparation of those

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compounds, E/Z isomers and tautomers and to their use in the control of pests, to pesticidal compositions in which the active ingredient has been selected from those compounds, E/Z isomers and tautomers, and to a process for the preparation of those compositions and to their use, to intermediates and, where applicable, their possible E/Z isomers, E/Z isomeric mixtures and/or tautomers, in free form or in salt form, for the preparation of those compounds, where applicable to tautomers, in free form or in salt form, of those intermediates and to a process for the preparation of those intermediates and their tautomers and to their use.

Certain dihaloallyl derivatives are proposed in the literature as active ingredients in pesticidal compositions. The biological properties of those known compounds are not entirely satisfactory in the field of pest control, however, for which reason there is a need to provide further compounds having pesticidal properties, especially for controlling insects and members of the order Acarina, that problem being solved according to the invention by the provision of the present compounds of formula (I).

The compounds of formula (I) and, where applicable, their tautomers are able to form salts, e.g. acid addition salts. The latter are formed, for example, with strong inorganic acids, such as mineral acids, e.g. sulfuric acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted or substituted, e.g. halo-substituted, C₁-C₄alkanecarboxylic acids, for example acetic acid, saturated or unsaturated dicarboxylic acids, e.g. oxalic, malonic, maleic, fumaric or phthalic acid, hydroxycarboxylic acids, e.g. ascorbic, lactic, malic, tartaric or citric acid, or benzoic acid, or with organic sulfonic acids, such as unsubstituted or substituted, e.g. halo-substituted, C₁-C₄alkane- or aryl-sulfonic acids, e.g. methane- or p-toluene-sulfonic acid. Furthermore, compounds of formula (I) having at least one acid group are able to form salts with bases. Suitable salts with bases are, for example, metal salts, such as alkali metal or alkaline earth metal salts, e.g. sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine, e.g. ethyl-, diethyl-, triethylor dimethyl-propyl-amine, or a mono-, di- or tri-hydroxy-lower alkylamine, e.g. mono-, di- or tri-ethanclamine. It may also be possible for corresponding internal salts to be formed. The free form is preferred. Of the salts of compounds of formula (I), preference is given to agrochemically advantageous salts. Hereinabove and hereinbelow any reference to the free compounds of formula (I) or to their salts is to be understood as including, where appropriate, the corresponding salts or the free compounds of formula (I), respectively. The same applies to tautomers of compounds of formula (I) and their salts.

The general terms used hereinabove and hereinbelow have the meanings given below, unless defined otherwise.

Halogen, as a group *per se* and as a structural element of other groups and compounds, such as of haloalkyl, halocycloalkyl, haloalkenyl, haloalkynyl and haloalkoxy, is fluorine, chlorine, bromine or iodine, especially fluorine, chlorine or bromine, more especially fluorine or chlorine, especially chlorine.

Unless defined otherwise, carbon-containing groups and compounds each contain from 1 up to and including 20, preferably from 1 up to and including 18, especially from 1 up to and including 10, more especially from 1 up to and including 6, especially from 1 up to and including 4, more especially from 1 up to and including 3, very especially 1 or 2, carbon atoms; methyl is especially preferred.

Alkylene is a straight-chain or branched bridging member and is especially -CH₂-, -CH₂CH₂-, -CH₂-CH₂-, -CH₂-CH₂-, -CH₂-CH₂-, -CH₂-CH₂-, -CH₂-CH₂-, -CH(CH₃)-, -CH(CH₃)CH₂-, -CH(CH₃)CH₂-, -CH(CH₃)CH(CH₃)- or -CH₂C(CH₃)₂-CH₂-.

Alkyl, as a group *per se* and as a structural element of other groups and compounds, such as of haloalkyl, alkoxy, alkoxyalkyl, haloalkoxy, alkoxycarbonyl, alkylthio, haloalkylthio, alkylsulfonyl and alkylsulfonyloxy, is - in each case giving due consideration to the number of carbon atoms contained in the group or compound in question - either straight-chain, e.g. methyl, ethyl, n-propyl, n-butyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-hexadecyl or n-octadecyl, or branched, e.g. isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Alkenyl and alkynyl - as groups *per se* and as structural elements of other groups and compounds, such as of haloalkenyl, haloalkynyl, alkenyloxy, haloalkenyloxy, alkynyloxy or haloalkynyloxy - are straight-chain or branched and each contains two or preferably one unsaturated carbon-carbon bond(s). There may be mentioned by way of example vinyl, prop-2-en-1-yl, 2-methylprop-2-en-1-yl, but-2-en-1-yl, but-3-en-1-yl, prop-2-yn-1-yl, but-2-yn-1-yl and but-3-yn-1-yl.

Cycloalkyl - as a group *per se* and as a structural element of other groups and compounds, such as of alkyl - is cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexyl, cyclopentyl or cyclooctyl. Cyclopentyl and cyclohexyl, and especially cyclopropyl, are preferred.

Halo-substituted carbon-containing groups and compounds, such as haloalkyl and haloalkoxy, may be partially halogenated or perhalogenated, the halogen substituents in the case of polyhalogenation being the same or different. Examples of haloalkyl - as a group per se and as a structural element of other groups and compounds, such as of haloalkoxy - are methyl substituted from one to three times by fluorine, chlorine and/or bromine, such as CHF2, CF3 or CH2CI; ethyl substituted from one to five times by fluorine, chlorine and/or bromine, such as CH₂CF₃, CF₂CF₃, CF₂CCl₃, CF₂CHCl₂, CF₂CHF₂, CF₂CFCl₂, CH₂CH₂Cl, CF₂CHBr₂, CF₂CHClF, CF₂CHBrF or CClFCHClF; propyl or isopropyl substituted from one to seven times by fluorine, chlorine and/or bromine, such as CH₂CHBrCH₂Br, CF₂CHFCF₃, CH₂CF₂CF₃, CF₂CF₂CF₃, CH(CF₃)₂ or CH₂CH₂CH₂CI; and butyl or an isomer thereof substituted from one to nine times by fluorine, chorine and/or bromine, such as $CF(CF_3)CHFCF_3$, $CF_2(CF_2)_2CF_3$ or $CH_2(CF_2)_2CF_3$.

Aryl is especially phenyl or naphthyl, preferably phenyl.

Heterocyclyl is to be understood as being a five- to seven-membered monocyclic ring containing from one to three hetero atoms selected from the group consisting of N, O and S, especially N and S, or a bicyclic ring system which may contain either in only one ring - such as, for example, in quinolinyl, quinoxalinyl, indolinyl, benzothiophenyl or benzofuranyl - or in both rings - such as, for example, in pteridinyl or purinyl - independently of one another, one or more hetero atoms selected from N, O and S. Preference is given to aromatic heterocycles, especially pyridyl, pyrimidyl, s-triazinyl, 1,2,4-triazinyl, tetrazolyl, thienyl, furanyl, tetrahydrofuranyl, pyranyl, tetrahydropyranyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, triazolyl, oxazolyl, isoxazolyl, thiadiazolyl, oxadiazolyl, benzothienyl, quinolinyl, quinoxalinyl, benzofuranyl, benzimidazolyl, benzpyrrolyl, benzthiazolyl, indolyl, coumarinyl and indazolyl, each of which is preferably bonded by way of a carbon atom; preference is given to thienyl, thiazolyl, benzofuranyl, benzothiazolyl, furanyl, tetrahydropyranyl or indolyl; especially pyridyl or thiazolyl.

Preferred embodiments within the scope of the invention are

- (2) compounds according to (1) of formula (I) wherein X₁ and X₂ are chlorine or bromine, especially chlorine;
- (3) compounds according to (1) or (2) of formula (I) wherein the group A₁-T-A₂ is a bond;
 - (4) compounds according to (1) to (3) of formula (I) wherein W is oxygen, -C(=O)O- or

- -C(=O)NH-, especially O;
- (5) compounds according to (1) to (4) of formula (I) wherein A_3 is a straight-chain alkylene bridge, especially ethylene, propylene or butylene, more especially propylene;
 - (6) compounds according to (1) to (5) of formula (I) wherein A₀ is a bond;
 - (7) compounds according to (1) to (6) of formula (I) wherein Q is oxygen;
 - (8) compounds according to (1) to (7) of formula (I) wherein Y is oxygen;
- (9) compounds according to (1) to (8) of formula (I) wherein R_1 and R_2 are bromine or chlorine, especially chlorine;
 - (10) compounds according to (1) to (9) of formula (I) wherein R₃ is hydrogen;
 - (11) compounds according to (1) to (10) of formula (I) wherein R₄ is hydrogen;
 - (12) compounds according to (1) to (11) of formula (I) wherein D is CH;
 - (13) compounds according to (1) to (11) of formula (I) wherein D is N;
- (14) compounds according to (1) to (13) of formula (I) wherein R_5 is C_1 - C_{12} alkoxy- C_1 - C_{12} alkyl;
 - (15) compounds according to (1) to (13) of formula (I) wherein R_{δ} is heterocyclyl;
- (16) compounds according to (1) to (13) of formula (I) wherein R_4 and the group $-C(=NOR_6)R_5$ are in the ortho-position relative to one another, R_4 and R_5 together form a C_2 - C_6 alkylene bridge wherein one or two CH_2 groups each independently of the other may have been replaced by O, NR_{12} , S or SO, and wherein the CH_2 groups are unsubstituted or mono- or di-substituted by halogen, OH, SH, CN, nitro, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 -alkoxy or C_1 - C_6 haloalkoxy;
 - (17) compounds according to (1) to (16) of formula (I) wherein M is O and
 - (18) compounds according to (1) to (16) of formula (I) wherein M is NOR₆.

Special preference is given to the compounds listed in the Tables.

The invention relates also to a process for the preparation of a compound of formula (I), or a salt thereof, wherein

(a) a compound of formula

$$\begin{bmatrix} R_{6} \\ O-N \\ R_{5} \end{bmatrix} = \begin{bmatrix} (R_{4})_{k} \\ R_{1} \\ R_{2} \end{bmatrix} = \begin{bmatrix} (R_{3})_{m} \\ R_{1} \\ R_{2} \end{bmatrix} \begin{bmatrix} Z_{1} \\ R_{2} \end{bmatrix} G$$
 (II)

wherein A_0 , A_1 , A_2 , A_3 , D, T, W, Q, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , m and k are as defined for formula (I) under (1), Z_1 is $-C(=O)R_{21}$ and R_{21} is H or C_1 - C_6 alkyl, is converted in the presence of an oxidising agent, especially a peracid, into a compound of formula

wherein Z_{2a} is O-C(=O)-C₁-C₆alkyl and G denotes the part of the formula in the brackets designated G in formula (II); either

(b) a compound of formula (IIIa) above or of formula

wherein G denotes the part of the formula in the brackets designated G in formula (II), Z_{2b} is a radical of formula $-Y-C(=O)R_{22}$, Y is as defined for formula (I) under (1), and R_{22} is C_1-C_{12} alkyl unsubstituted or substituted by from one to three identical or different halogen substituents, or is phenyl unsubstituted or substituted by from one to three identical or different substituents selected from halogen, CN, nitro, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 -alkylcarbonyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, C_1-C_6 alkoxycarbonyl and C_2-C_6 haloalkenyloxy, is converted by hydrolytic cleavage into a compound of formula

wherein G denotes the part of the formula in the brackets designated G in formula (II), Z_3 is YH, and Y is as defined for formula (I) under (1); or

(c) a compound of formula

$$G-Z_4(V)$$
,

wherein Z_4 is Y-CH₂-phenyl, wherein the phenyl radical is unsubstituted or substituted by from one to three identical or different substituents selected from halogen, CN, nitro, C_1 - C_6 alkyl, C_1 - C_6 alkyl, C_1 - C_6 alkyl, C_1 - C_6 alkyl, C_2 - C_6 alkoxy, C_1

part of the formula in the brackets designated G in formula (II), and Y is as defined for formula (I), is converted by removal of the benzyl group into a compound of formula (IV), as defined above;

(d) the compound of formula (IV) so obtained is reacted in the presence of a base with a compound of formula

wherein Hal is halogen, preferably bromine or chlorine, and alkyl is C_1 - C_6 alkyl, or the two alkyl radicals together form a C_3 - C_8 alkylene bridge, to form a compound of formula

$$G-Z_5$$
 (VI),

wherein G denotes the part of the formula in the brackets designated G in formula (II) and $Z_{\scriptscriptstyle{5}}$ is

wherein alkyl and Y are as defined above;

(e) the compound of formula (VI) so obtained is converted by deprotection of the acetal function in the presence of an acid into a compound of formula

wherein Z_6 is a group $-Y-CH_2-C(=O)H$, G is as defined above for the compound of formula (II), and Y is as defined for formula (I) under (1); <u>either</u>

- (f₁) for the preparation of a compound of formula (I) wherein X_1 and X_2 are chlorine or bromine, a compound of formula (VII) is reacted in the presence of a phosphine with a compound of formula $C(X)_4$ wherein X is chlorine or bromine; or
- (f_2) for the preparation of a compound of formula (I) wherein X_1 and X_2 are chlorine, a compound of formula (VII) is reacted first with CCl_3 -COOH or with chloroform in the presence of a strong base, then with acetic anhydride and subsequently with powdered zinc in acetic acid; or

- (f_3) for the preparation of a compound of formula (I) wherein X_1 is fluorine and X_2 is chlorine or bromine, a compound of formula (VII) is reacted first with a compound of the formula CF_2X_2 , of the formula CF_2X_3 , of the formula CF_2X_3 of the formula CF_2X_3 or of the formula CF_3X_3 o
- (g_1) for the preparation of a compound of formula (I) wherein X_1 and X_2 are chlorine or bromine, a compound of formula (IV) is reacted in the presence of a base with a compound of formula

wherein L_3 is a leaving group, preferably chlorine or bromine, and Hal is chlorine or bromine; or

 (g_2) for the preparation of a compound of formula (I) wherein X_1 and X_2 are chlorine or bromine, a compound of formula (IV) is reacted in the presence of a base with a compound of the formula

wherein Hal is halogen and X is chlorine or bromine.

The invention relates also to

(h) a process for the preparation of a compound of formula (I), as defined under (1), and wherein Q is O, NR_{11} or S, and R_{11} is as defined for formula (I) under (1), wherein a compound of formula

$$R_{6}$$
 $O-N$
 A_{0}
 A_{1}
 A_{1}
 A_{2}
 A_{3}
 A_{1}
 A_{3}
 A_{1}
 A_{3}
 A_{4}
 A_{5}
 A_{5}
 A_{1}
 A_{1}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{1}
 A_{1}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}

wherein A_0 , A_1 , A_2 , A_3 , D, T, W, R_4 , R_5 , R_6 and k are as defined for formula (I) under (1) and L_1 is a leaving group, is reacted in the presence of a base with a compound of formula

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$$R_1$$
 R_3)m
 Z
 $H-Q$
 R_2
 $(IX),$

wherein R_1 , R_2 , R_3 and m are as defined for formula (I) under (1), Q is O, NR_{11} or S and Z is one of the radicals Z_1 to Z_6 as defined for the above formulae (II) to (VII), and R_{11} is as defined for formula (I) under (1), and the resulting compound of formula

$$R_{6}$$
 $O-N$
 A_{0}
 A_{1}
 A_{1}
 A_{2}
 A_{3}
 A_{3}
 A_{2}
 A_{3}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{1}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}

wherein A_0 , A_1 , A_2 , A_3 , D, T, W, Q, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , m and k are as defined for formula (I) under (1) and Z is one of the radicals Z_1 to Z_6 as defined for formulae (II) to (VII) indicated above, is, as necessary, that is to say according to the meaning of the radical Z, reacted further analogously to one or more of process steps (a) to (g).

In the compounds of formulae X/a to X/f, Z in compound X/a has the same meanings as Z_1 in the compound of formula (II), and Z in compound X/b has the same meanings as Z_2 as defined for formula (III), and so on.

The invention relates also to

(i₁) a process for the preparation of a compound of formula (I) as defined above wherein W is O, NR_{11} , S, -O-C(=O)- or $-NR_{11}$ -C(=O)- and R_{11} is as defined for formula (I) under (1), wherein a compound of formula

$$R_{6}$$
 $O-N$
 A_{0}
 A_{1}
 A_{1}
 A_{2}
 A_{1}
 A_{1}
 A_{2}
 A_{1}
 A_{2}
 A_{1}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}
 A_{5}
 A_{1}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{7}
 A_{7}

wherein A_0 , A_1 , A_2 , A_3 , D, T, W, R_4 , R_5 , R_6 , m and k are as defined for formula (I) under (1), W_1 is O, NR_{11} or S and R_{11} is as defined for formula (I) under (1), is reacted with a compound of formula

wherein A₃, R₁, R₂, R₃, Q and m are as defined for formula (I) under (1), L₂ is a leaving group or a group Hal-C(=O)- wherein Hal is a halogen atom, preferably chlorine or bromine, and Z is one of the radicals Z_1 to Z_6 as defined in formulae (II) to (VII) indicated above; or

(i₂) for the preparation of a compound of formula (I) as defined above wherein W is O, NR₁₁, S, -C(=O)-O- or -C(=O)-NR₁₁- and R₁₁ is as defined for formula (I) under (1), wherein a compound of formula

$$R_{6}$$
 $O-N$
 A_{0}
 A_{1}
 A_{1}
 A_{2}
 A_{1}
 A_{2}
 A_{1}
 A_{2}
 A_{1}
 A_{2}
 A_{3}
 A_{4}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{5}
 A_{7}
 A_{7}

wherein A₀, A₁, A₂, D, T, R₄, R₅, R₆ and k are as defined for formula (I) under (1), and L₁ is a leaving group or a group -C(=O)-Hal wherein Hal is a halogen atom, preferably chlorine or bromine, is reacted with a compound of formula

$$R_1$$
 X_2 X_3 X_4 X_4

wherein W_2 is O, NR_{11} or S and R_1 , R_2 , R_3 , R_{11} and m are as defined for formula (I) under (1),

and a resulting compound of formula (Xa) to (Xf) as defined above is, as necessary, that is to say according to the meaning of the radical Z, reacted further analogously to one or more of process steps (a) to (g).

In the compounds of formulae XII/a to XII/f and XIV/a to X!V/f, the radicals Z are as defined above for the compounds X/a to X/f; that is to say, for example, Z in the compound of formula XII/a has the same meanings as Z₁ in the compound of formula (II), and Z in compound XII/b has the same meanings as Z₂ as defined for formula (III), and so on.

The invention relates also to

(k) a process for the preparation of a compound of formula (I) as defined above under (1), wherein a compound of formula (VIII) as defined above is reacted in the presence of a base with a compound of formula

$$R_1$$
 X_2
 X_1
 X_2
 X_2
 X_3
 X_4
 X_2
 X_3
 X_4
 X_2
 X_4
 X_4
 X_4
 X_5
 X_5
 X_7
 X_8
 X_8
 X_9
 X_9

wherein R₁, R₂, R₃, Q, X₁, X₂, Y and m are as defined for formula (I) under (1).

The invention relates also to

(I) a process for the preparation of a compound of formula (I) as defined above under (1), wherein a compound of formula (XI) as defined above is reacted in a manner analogous to process variant (i1) or (i2) with a compound of formula

wherein A_3 , R_1 , R_2 , R_3 , Q, Y, X_1 , X_2 and m are as defined for formula (I) under (1) and L_2 is as defined for formula (XII).

The compounds of formulae (IIIa) and (IIIb) wherein R₁ and R₂ are halogen can be obtained by

(m₁) reacting a compound of formula

$$H \rightarrow \begin{pmatrix} R_3 \end{pmatrix}_m Y - H$$
 $H - Q \rightarrow H$
 $(XVII),$

wherein R₃, Q, Y and m are as defined for formula (I) under (1), with a compound of the formula Hal-C(=O)-phenyi and Hal is a halogen atom, preferably chlorine or bromine;

(m₂) halogenating the resulting compound of formula

$$H \rightarrow \begin{pmatrix} R_3 \end{pmatrix}_m Y^- C(=O)$$
-phenyl (XVIII),

wherein R_3 , Q, Y and m are as defined for formula (I) under (1), and further reacting the resulting compound of formula

$$R_1$$
 Y
 $C(=O)$ -phenyl
 (XIX) ,

wherein R_3 , Q, Y and m are as defined for formula (I) under (1) and R_1 and R_2 are halogen, analogous to Process (k).

The invention relates also to a process for the preparation of a compound of formula (I) as defined above, wherein

(n1) a compound of formula

$$\begin{array}{c}
O \\
R_{5}
\end{array}$$

$$\begin{array}{c}
(R_{4})_{k} \\
R_{1}
\end{array}$$

$$\begin{array}{c}
(R_{3})_{m} \\
R_{1}
\end{array}$$

$$\begin{array}{c}
(R_{3})_{m} \\
X_{2}
\end{array}$$

$$\begin{array}{c}
X_{2}
\end{array}$$

$$\begin{array}{c}
(XX)_{n}
\end{array}$$

wherein A_0 , A_1 , A_2 , A_3 , D, T, W, Q, R_1 , R_2 , R_3 , R_4 , R_5 , m and k are as defined for formula (I) under (1), is reacted with a compound of the formula R_6 -O-NH₂ wherein R_6 is as defined for formula (I) under (1), or with a salt thereof; or

(n2) a compound of formula (XX) above is reacted first with hydroxylamine, or with a salt thereof, to form a compound of formula (I) wherein R_{θ} is hydrogen, and then optionally reacted further with an alkylating agent, preferably with an alkyl halide such as methyl iodide or ethyl iodide.

The invention relates also to a process for the preparation of a compound of formula (I) as defined above wherein R_5 is alkyl that carries a halogen or an alkoxy in the α -position, wherein

(o) a compound of formula

$$\begin{array}{c} O \\ A_0 \\ \hline \end{array} \begin{array}{c} (R_4)_k \\ A_1 \\ \hline \end{array} T \\ \hline \end{array} \begin{array}{c} (R_3)_m \\ A_2 \\ \hline \end{array} \begin{array}{c} (R_3)_m \\ X_2 \end{array} \begin{array}{c} (XXIII) \\ \end{array}$$

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or a compound of formula

$$\begin{array}{c} R_{6} \\ O \\ N \\ O \\ A_{0} \\ \hline \end{array} \begin{array}{c} (R_{4})_{k} \\ A_{1} \\ \hline \end{array} \begin{array}{c} R_{1} \\ \hline \end{array} \begin{array}{c} (R_{3})_{m} \\ X_{2} \\ \hline \end{array} \begin{array}{c} (Ia)_{k} \\ R_{56} \\ \hline \end{array}$$

wherein A₀, A₁, A₂, A₃, D, T, W, Q, R₁, R₂, R₃, R₄, R₆, m and k are as defined for formula (I) under (1) and R_{55} is C_1 - C_{11} alkyl, is reacted with a halogenating agent, and the resulting compound of formula

$$\begin{array}{c} O \\ A_0 \\ \hline \end{array} \begin{array}{c} (R_4)_k \\ A_1 \\ \hline \end{array} T \\ -A_2 \\ \hline \end{array} W \\ -A_3 \\ \hline \end{array} Q \begin{array}{c} (R_3)_m \\ X_2 \\ \hline \\ R_2 \end{array} (XXIIIa),$$

or of formula

$$\begin{array}{c} R_{6} \\ O \\ N \\ O \\ A_{0} \\ \hline \end{array} \begin{array}{c} (R_{4})_{k} \\ A_{1} \\ \hline \end{array} \begin{array}{c} (R_{3})_{m} \\ A_{3} \\ \hline \end{array} \begin{array}{c} (R_{3})_{m} \\ X_{2} \\ \hline \end{array} \begin{array}{c} (Ib), \\ \end{array}$$

wherein A_0 , A_1 , A_2 , A_3 , D, T, W, Q, R_1 , R_2 , R_3 , R_4 , R_{55} , R_6 , m and k are as defined for formula (XXIIIa) and R is halogen, or

(p) a compound of formula (lb) is reacted with an alcohol or with an alcoholate.

The invention relates also to a process for the preparation of a compound of formula (I) as defined above wherein R5 is -C(=O)-O-R8, -C(=O)-R9 or -C(=O)-NH-R9 and R8, R9 and R10 are as defined for formula (I) under (1), wherein

(q) a compound of formula

$$\begin{array}{c} & & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

wherein R_{56} is -C(=O)-O-R₈, -C(=O)-R₉ or -C(=O)-NH-R₉ and R₈, R₉, R₁₀ and the other symbols are as defined for formula (I) under (1), is converted to an oxime with an alkyl nitrite to form a compound of formula (I) wherein R_5 is -C(=O)-O-R₈, -C(=O)-R₉ or -C(=O)-NH-R₉, and R_8 , R_9 and R_{10} are as defined for formula (I) under (1) and R_6 is hydrogen, and the resulting compound of formula (I) is optionally alkylated analogously to Process step (n2).

It will be understood that the processes (n) to (q) according to the invention can also be carried out on any precursor and such a precursor can then be processed in accordance with Processes (a) to (m) to form compounds of formula (I). The invention relates also to corresponding intermediates; they are, where novel, the compounds of formulae (II) to (XXVI), in free form or in salt form, and the compounds of formulae

$$E \xrightarrow{(R_4)_k} A_1 - T - A_2 - W - A_3 - L_1 \quad (XXVIII),$$

$$E \xrightarrow{(R_4)_k} A_1 - T - A_2 - W_1 - H \quad (XXVIIII) \text{ and}$$

$$E \xrightarrow{(R_4)_k} A_1 - T - A_2 - L_1 \quad (XXIX),$$

wherein A₁, A₂, A₃, L₁, D, T, W₁, R₄, d and k are as defined above and E is halogen or a group -CHO, -C(=O)-alkyl or -C(=O)-O-alkyl. It will be understood that, for further processing, such intermediates may need to be protected by protecting groups, for example a keto function may be protected in ketal form.

The compounds of formula la, lb, ll, VIII, X/a to X/f, XI, XIII, XX, XXIII, XXIIIa are new and form also a part of the invention.

The preferences applying to those intermediates of formulae (II) to (XXIX) are the same as those defined for the compounds of formula (I) under (2) to (13), as appropriate.

The reactions described hereinabove and hereinbelow are carried out in a manner known *per se*, for example in the absence or, if necessary, in the presence of a suitable solvent or diluent or of a mixture thereof, the reactions being carried out, as required, with cooling, at room temperature or with heating, for example in a temperature range of approximately from -80°C to the boiling temperature of the reaction mixture, preferably from approximately -20°C to approximately +150°C, and, if necessary, in a closed vessel, under pressure, under an inert gas atmosphere and/or under anhydrous conditions. Especially advantageous reaction conditions can be found in the Examples.

A leaving group, for example the leaving groups L_1 and L_2 defined above, or a counterion is to be understood hereinbefore and hereinbelow as being any removable group that customarily comes into consideration for chemical reactions, such as are known to the person skilled in the art; especially OH, halogens, such as fluorine, chlorine, bromine, iodine, $-O-Si(C_1-C_8alkyl)_3$, -O-aryl, $-S-(C_1-C_8alkyl)$, -S-aryl, $-O-S(=O)_2U$, -S(=O)U or $-S(=O)_2U$, wherein U is unsubstituted or substituted C_1-C_8alkyl , $C_2-C_8alkenyl$, $C_2-C_8alkynyl$, unsubstituted or substituted aryl or unsubstituted or substituted benzyl. Especially preferred as leaving group are chlorine or bromine, mesylate, triflate, tosylate, especially chlorine; or chloride or bromide, especially chloride.

<u>Process (a):</u> The reaction is carried out in acetic acid or a halogenated hydrocarbon, such as dichloromethane, at temperatures of from –20°C to 100°C, preferably at from 20°C to 50°C. As oxidising agents there are used, for example, hydrogen peroxide, a peracid, such as peracetic acid, trifluoroperacetic acid, 3-chloroperbenzoic acid or a mixture, such as sodium perborate in acetic acid.

<u>Process (b)</u>: The reaction is preferably carried out in an alcohol, such as methanol, ethanol or an alcohol/water mixture, in the presence of an inorganic base, such as NaOH or KOH, and at temperatures of from 0°C to 150°C, preferably from 20°C to 80°C. Alternatively aminolysis with a primary amine, such as n-butylamine, can be carried out in a hydrocarbon, such as toluene or benzene, at temperatures of from 0°C to 150°C, preferably at from 20°C to 80°C.

<u>Process (c):</u> Depending upon the nature of the benzyl substituent to be removed, the reaction can be carried out, for example, under a hydrogen atmosphere, at from 1 to 150 bar, especially at from 1 to 20 bar, and with the addition of a catalyst, such as palladium / carbon, in an alcohol or ether. The preferred reaction temperature is from 0°C to 120°C, especially from 20°C to 80°C.

<u>Processes (d) and (g)</u>: The reaction is preferably carried out in the presence of a base, such as potassium or sodium carbonate, in acetone or dimethylformamide, at temperatures of from 0°C to 150°C, preferably from 20°C to 80°C. If necessary, catalytic amounts of potassium iodide or sodium iodide, or phase transfer catalysts, such as crown ethers or quaternary ammonium salts, are added.

<u>Process (e)</u>: The reaction is preferably carried out in acetone, dichloromethane, acetic acid, or especially in water, optionally with the addition of a mineral acid, at temperatures of from 0°C to 120°C, preferably at from 20°C to 50°C. For complete cleavage of the acetal it is preferable to add a strong mineral acid, for example hydrochloric acid, sulfuric acid or 4-toluenesulfonic acid.

Process (f): For the preparation of the difluoro-, dichloro-, dibromo-, chlorofluoro- and bromofluoro-vinyl compounds, reaction with CCl₄, CBr₄, CF₂X₂, CFX₃, CF₂XC(=O)ONa or CFX₂C(=O)ONa wherein X is bromine or chlorine is carried out in the presence of a trialkylor triaryl-phosphine, optionally with the addition of powdered zinc. The reaction is carried out in an inert solvent such as, for example, benzene or toluene, or an ether, such as diethyl ether, diisopropyl ether, dioxane or tetrahydrofuran, at temperatures of from 0°C to 150°C, preferably at from 20°C to 80°C.

For the preparation of the dichlorovinyl compounds it is also possible for the process to be carried out in dimethylformamide, benzene, toluene, or in an ether, at temperatures of from 0°C to 120°C, preferably from 20°C to 80°C, and in the presence of trichloroacetic acid/sodium trichloroacetate, then by addition of acetic anhydride, optionally with the addition of base, for example triethylamine, and finally by addition of zinc and acetic acid.

<u>Processes (h) and (k)</u>: The reaction is preferably carried out in an ether, dimethylformamide, dimethylacetamide or N-methylpyrrolidone, at temperatures of from 0°C to 150°C, preferably at from 20°C to 80°C, with the addition of a base, such as potassium or sodium carbonate. Alternatively a coupling reagent, for example azodicarboxylic acid diethyl or diisopropyl ester and triphenylphosphine, can be used.

<u>Processes (i) and (I):</u> Where L₂ is a group Hal-C(=O)-, the process can be carried out in an inert solvent, such as in an ether or in toluene, at from 0°C to 80°C, and in the presence of a suitable base, for example a trialkylamine.

In the other cases the reaction is carried out in an ether, in an amide such as dimethyl-formamide or N-methylpyrrolidone, and at from 0°C to 150°C. Sodium hydride, for example, can be used as base.

Process (m₁): The reaction is preferably carried out in a solvent, such as dioxane, dichloromethane, acetonitrile or toluene, at from 0 to 100°C, and in the presence of a base.

<u>Process (m₂):</u> The reaction is preferably carried out in water or a chlorinated hydrocarbon and with a halogenating agent, such as chlorine, bromine, NaOCI or tert-butyl hypochlorite.

<u>Process (n):</u> The reaction is preferably carried out in an alcohol, such as methanol, ethanol or isopropanol, in an amide, such as dimethylformamide, in dimethyl sulfoxide, in an ether, such as tetrahydrofuran, or in an organic base, such as a trialkylamine. The preferred working temperature is from 0°C to 180°C, especially from 20°C to 100°C.

<u>Process (o):</u> Preferred halogenating agents are chlorine, bromine and CuBr₂. Suitable solvents are especially halogenated hydrocarbons, such as carbon tetrachloride or methylene chloride, and also esters, such as ethyl acetate. The preferred working temperature is from 0°C to 180°C, especially from 20°C to 100°C.

<u>Process (p):</u> Suitable solvents are especially halogenated hydrocarbons, such as carbon tetrachloride or methylene chloride, and also ethers, such as tetrahydrofuran or dioxane, amides such as dimethylformamide or dimethyl sulfoxide. Alkyl nitrites that come into consideration are especially tert-butyl nitrite and isopentyl nitrite. The reaction is preferably carried out in the presence of hydrochloric acid.

The invention relates especially to the preparation processes described in Examples P1 to P8.

Compounds of formula (I) obtainable in accordance with the process or by other means can be converted into other compounds of formula (I) in a manner known *per se* by replacement of one or more substituents in the starting compound of formula (I) in customary manner by another (other) substituent(s) according to the invention.

In the case of such replacement, depending upon the choice of reaction conditions and starting materials suitable therefor, it is possible for only one substituent to be replaced by another substituent according to the invention in a reaction step or for a plurality of substituents to be replaced by other substituents according to the invention in the same reaction step.

Salts of compounds of formula (I) can be prepared in a manner known *per se*. For example, salts of compounds of formula (I) with bases are obtained by treatment of the free compounds with a suitable base or with a suitable ion exchange reagent.

Salts of compounds of formula (I) can be converted into the free compounds of formula (I) in customary manner, for example by treatment with a suitable acid or with a suitable ion exchange reagent.

Salts of compounds of formula (I) can be converted in a manner known *per se* into other salts of a compound of formula (I).

The compounds of formula (I), in free form or in salt form, may be in the form of one of the possible isomers or in the form of a mixture thereof, for example, depending upon the number of asymmetric carbon atoms occurring in the molecule and their absolute and relative configuration, and/or depending upon the configuration of non-aromatic double bonds occurring in the molecule, in the form of pure isomers, such as enantiomers and/or diastereoisomers, or in the form of mixtures of isomers, such as mixtures of enantiomers, for example racemates, mixtures of diastereoisomers or mixtures of racemates. The invention relates both to the pure isomers and to all possible mixtures of isomers and is to be interpreted as such hereinbefore and hereinafter, even if stereochemical details are not mentioned specifically in every case.

Mixtures of diastereoisomers, mixtures of racemates and mixtures of double bond isomers of compounds of formula (I), in free form or in salt form, that are obtainable by the process according to the invention – depending upon the starting materials and procedures chosen – or by some other method, can be separated into the pure diastereoisomers or racemates in known manner on the basis of the physico-chemical differences between the constituents, for example by means of fractional crystallisation, distillation and/or chromatography.

Mixtures of enantiomers, such as racemates, that are obtainable in a corresponding manner can be resolved into the enantiomers by known methods, for example by recrystallisation from an optically active solvent, by chromatography on chiral adsorbents, for example high pressure liquid chromatography (HPLC) on acetylcellulose, with the aid of suitable microorganisms, by cleavage with specific, immobilised enzymes, *via* the formation of inclusion compounds, for example using chiral crown ethers, only one enantiomer being complexed, or by conversion into diastereoisomeric salts and separation of the mixture of diastereoisomers so obtained, for example on the basis of their different solubilities by

fractional crystallisation, into the diastereoisomers, from which the desired enantiomer can be freed by the action of suitable agents.

Apart from by separation of corresponding mixtures of isomers, it is also possible for pure diastereoisomers or enantiomers to be obtained according to the invention by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process according to the invention using starting materials having correspondingly suitable stereochemistry.

In each case it is advantageous to isolate or synthesise the biologically more active isomer, e.g. enantiomer or diastereoisomer, or mixture of isomers, e.g. mixture of enantiomers or mixture of diastereoisomers, where the individual components have different biological activity.

The compounds of formula (I), in free form or salt form, can also be obtained in the form of their hydrates and/or may include other solvents, for example solvents which may have been used for the crystallisation of compounds present in solid form.

The invention relates to all those embodiments of the process according to which a compound obtainable as starting material or intermediate at any stage of the process is used as starting material and some or all of the remaining steps are carried out or a starting material is used in the form of a derivative or salt and/or its racemates or enantiomers or, especially, is formed under the reaction conditions.

In the process of the present invention it is preferable to use those starting materials and intermediates, in each case in free form or in salt form, which result in the compounds of formula (I) and their salts described at the beginning as being especially valuable.

In the area of pest control, the compounds of formula (I) according to the invention are active ingredients exhibiting valuable preventive and/or curative activity with a very advantageous biocidal spectrum even at low rates of concentration, while being well tolerated by warm-blooded animals, fish and plants. The active ingredients according to the invention are effective against all or individual development stages of normally sensitive animal pests, but also of resistant animal pests, such as insects and members of the order Acarina. The insecticidal or acaricidal activity of the active ingredients according to the invention may manifest itself directly, i.e. in the mortality of the pests, which occurs immediately or only after some time, for example during moulting, or indirectly, for example in reduced ovi-

position and/or hatching rate, good activity corresponding to a mortality of at least 50 to 60 %.

Successful control within the scope of the subject of the invention is possible, in particular, of pests from the orders Lepidoptera, Coleoptera, Orthoptera, Isoptera, Psocoptera, Anoplura, Mallophaga, Thysanoptera, Heteroptera, Homoptera, Hymenoptera, Diptera, Siphonaptera, Thysanura and Acarina, mainly Lepidoptera and Coleoptera. Very especially good control is possible of the following pests:

Abagrotis spp., Abraxas spp., Acantholeucania spp., Acanthoplusia spp., Acarus spp., Acarus siro, Aceria spp., Aceria sheldoni, Acleris spp., Acoloithus spp., Acompsia spp., Acossus spp., Acria spp., Acrobasis spp., Acrocercops spp., Acrolepia spp., Acrolepiopsis spp., Acronicta spp., Acropolitis spp., Actebia spp., Aculus spp., Aculus schlechtendali, Adoxophyes spp., Adoxophyes reticulana, Aedes spp., Aegeria spp., Aethes spp., Agapeta spp., Agonopterix spp., Agriopis spp., Agriotes spp., Agriphila spp., Agrochola spp., Agroperina spp., Alabama ssp., Alabama argillaceae, Agrotis spp., Albuna spp., Alcathoe spp., Alcis spp., Aleimma spp., Aletia spp., Aleurothrixus spp., Aleurothrixus floccosus, Aleyrodes spp., Aleyrodes brassicae, Allophyes spp., Alsophila spp., Amata spp., Amathes spp., Amblyomma spp., Amblyptilia spp., Ammoconia spp., Amorbia spp., Amphion spp., Amphipoea spp., Amphipyra spp., Amyelois spp., Anacamptodes spp., Anagrapha spp., Anarsia spp., Anatrychyntis spp., Anavitrinella spp., Ancylis spp., Andropolia spp., Anhimella spp., Antheraea spp., Antherigona spp., Antherigona soccata, Anthonomus ssp., Anthonomus grandis, Anticarsia spp., Anticarsia gemmatalis, Aonidiella spp., Apamea spp., Aphania spp., Aphelia spp., Aphididae, Aphis spp., Apotomis spp., Aproaerema spp., Archippus spp., Archips spp., Acromyrmex, Arctia spp., Argas spp., Argolamprotes spp., Argyresthia spp., Argyrogramma spp., Argyroploce spp., Argyrotaenia spp., Arotrophora spp., Ascotis spp., Aspidiotus spp., Aspilapteryx spp., Asthenoptycha spp., Aterpia spp., Athetis spp., Atomaria spp., Atomaria linearis, Atta spp., Atypha spp., Autographa spp., Axylia spp., Bactra spp., Barbara spp., Batrachedra spp., Battaristis spp., Bembecia spp., Bemisia spp., Bemisia tabaci, Bibio spp., Bibio hortulanis, Bisigna spp., Blastesthia spp., Blatta spp., Blatella spp., Blepharosis spp., Bleptina spp., Boarmia spp., Bombyx spp., Bomolocha spp., Boophilus spp., Brachmia spp., Bradina spp., Brevipalpus spp., Brithys spp., Bryobia spp., Bryobia praetiosa, Bryotropha spp., Bupalus spp., Busseola spp., Busseola fusca, Cabera spp., Cacoecimorpha spp., Cadra spp., Cadra cautella, Caenurgina spp., Calipitrimerus spp., Callierges spp., Callophpora spp., Callophpora erythrocephala, Calophasia spp., Caloptilia spp., Calybites spp., Capnoptycha spp., Capua spp., Caradrina spp., Caripeta spp., Car-

menta spp., Carposina spp., Carposina nipponensis, Catamacta spp., Catelaphris spp., Catoptria spp., Caustoloma spp., Celaena spp., Celypha spp., Cenopis spp., Cephus spp., Ceramica spp., Cerapteryx spp., Ceratitis spp, Ceratophyllus spp., Ceroplaster spp., Chaetocnema spp., Chaetocnema tibialis, Chamaesphecia spp., Charanvca spp., Cheimophila spp., Chersotis spp., Chiasmia spp., Chilo spp., Chionodes spp., Chorioptes spp., Choristoneura spp., Chrysaspidia spp., Chrysodeixis spp., Chrysomya spp., Chrysomphalus spp., Chrysomphalus dictyospermi, Chrysomphalus aonidium, Chrysoteuchia spp., Cilix spp., Cimex spp., Clysia spp., Clysia ambiguella, Clepsis spp., Cnaemidophorus spp., Cnaphalocrocis spp., Cnephasia spp., Coccus spp., Coccus hesperidum, Cochylis spp., Coleophora spp., Colotois spp., Commophila spp., Conistra spp., Conopomorpha spp., Corcyra spp., Cornutiplusia spp., Cosmia spp., Cosmopolites spp., Cosmopterix spp., Cossus spp., Costaeonvexa spp., Crambus spp., Creatonotos spp., Crocidolomia spp., Crocidolomia binotalis, Croesia spp., Crymodes spp., Cryptaspasma spp., Cryptoblabes spp., Cryptocala spp., Cryptophlebia spp., Cryptophlebia leucotreta, Cryptoptila spp., Ctenopseustis spp., Cucullia spp., Curculio spp., Culex spp., Cuterebra spp., Cydia spp., Cydia pomonella, Cymbalophora spp., Dactylethra spp., Dacus spp., Dadica spp., Damalinea spp., Dasychira spp., Decadarchis spp., Decodes spp., Deilephila spp., Deltodes spp., Dendrolimus spp., Depressaria spp., Dermestes spp., Dermanyssus spp., Dermanyssus gallinae, Diabrotica spp., Diachrysia spp., Diaphania spp., Diarsia spp., Diasemia spp., Diatraea spp., Diceratura spp., Dichomeris spp., Dichrocrocis spp., Dichrorampha spp., Dicycla spp., Dioryctria spp., Diparopsis spp., Diparopsis castanea, Dipleurina spp., Diprion spp., Diprionidae, Discestra spp., Distantiella spp., Distantiella theobroma, Ditula spp., Diurnea spp., Doratopteryx spp., Drepana spp., Drosphila spp., Drosphila melanogaster, Dysauxes spp., Dysdercus spp., Dysstroma spp., Eana spp., Earias spp., Ecclitica spp., Ecdytolopha spp., Ecpyrrhorrhoe spp., Ectomyelois spp., Eetropis spp., Egira spp., Elasmopalpus spp., Emmelia spp., mpoasca spp., Empyreuma spp., Enargia spp., Enarmonia spp., Endopiza spp., Endothenia spp., Endotricha spp., Eoreuma spp., Eotetranychus spp., Eotetranychus carpini, Epagoge spp., Epelis spp., Ephestia spp., Ephestiodes spp., Epiblema spp., Epiehoristodes spp., Epinotia spp., Epiphyas spp., Epiplema spp., Epipsestis spp., Epirrhoe spp., Episimus spp., Epitymbia spp., Epllachna spp., Erannis spp., Erastria spp., Eremnus spp., Ereunetis spp., Eriophyes spp., Eriosoma spp., Eriosoma lanigerum, Erythroneura spp., Estigmene spp., Ethmia spp., Etiella spp., Euagrotis spp., Eucosma spp., Euchlaena spp., Euclidia spp., Eucosma spp., Euchistus spp., Eucosmomorpha spp., Eudonia spp., Eufidonia spp., Euhyponomeutoides spp., Eulepitodes spp., Eulia spp., Eulithis spp., Eupithecia spp., Euplexia spp., Eupoecilia

spp., Eupoecilia ambiguella, Euproctis spp., Eupsilia spp., Eurhodope spp., Eurois spp., Eurygaster spp., Eurythmia spp., Eustrotia spp., Euxoa spp., Euzophera spp., Evergestis spp., Evippe spp., Exartema spp., Fannia spp., Faronta spp., Feltia spp., Filatima spp., Fishia spp., Frankliniella spp., Fumibotys spp., Gaesa spp., Gasgardia spp., Gastrophilus spp., Gelechia spp., Gilpinia spp., Gilpinia polytoma, Glossina spp., Glyphipterix spp., Glyphodes spp., Gnorimoschemini spp., Gonodonta spp., Gortyna spp., Gracillaria spp., Graphania spp., Grapholita spp., Grapholitha spp., Gravitarmata spp., Gretchena spp., Griselda spp., Gryllotalpa spp., Gynaephora spp., Gypsonoma spp., Hada spp., Haematopinus spp., Halisidota spp., Harpipteryx spp., Harrisina spp., Hedya spp., Helicoverpa spp., Heliophobus spp., Heliothis spp., Hellula spp., Helotropa spp., Hemaris spp., Hercinothrips spp., Herculia spp., Hermonassa spp., Heterogenea spp., Holomelina spp., Homadaula spp., Homoeosoma spp., Homoglaea spp., Homohadena spp., Homona spp., Homonopsis spp., Hoplocampa spp., Hoplodrina spp., Hoshinoa spp., Hxalomma spp., Hydraecia spp., Hydriomena spp., Hyles spp., Hyloicus spp., Hypagyrtis spp., Hypatima spp., Hyphantria spp., Hyphantria cunea, Hypocala spp., Hypocoena spp., Hypodema spp., Hyppobosca spp., Hypsipyla spp., Hyssia spp., Hysterosia spp., Idaea spp., Idia spp., Ipimorpha spp., Isia spp., Isochorista spp., Isophrictis spp., Isopolia spp., Isotrias spp., Ixodes spp., Itame spp., Jodia spp., Jodis spp., Kawabea spp., Keiferia spp., Keiferia lycopersicella, Labdia spp., Lacinipolia spp., Lambdina spp., Lamprothritpa spp., Laodelphax spp., Lasius spp., Laspeyresia spp., Leptinotarsa spp., Leptinotarsa decemlineata, Leptocorisa spp., Leptostales spp., Lecanium spp., Lecanium comi, Lepidosaphes spp., Lepisma spp., Lepisma saccharina, Lesmone spp., Leucania spp., Leucinodes spp., Leucophaea spp., Leucophaea maderae, Leucoptera spp., Leucoptera scitella, Linognathus spp., Liposcelis spp., Lissorhoptrus spp., Lithacodia spp., Lithocolletis spp., Lithomoia spp., Lithophane spp., Lixodessa spp., Lobesia spp., Lobesia botrana, Lobophora spp., Locusta spp., Lomanaltes spp., Lomographa spp., Loxagrotis spp., Loxostege spp., Lucilia spp., Lymantria spp., Lymnaecia spp., Lyonetia spp., Lyriomyza spp., Macdonnoughia spp., Macrauzata spp., Macronoctua spp., Macrosiphus spp., Malacosoma spp., Maliarpha spp., Mamestra spp., Mamestra brassicae, Manduca spp., Manduca sexta, Marasmia spp., Margaritia spp., Matratinea spp., Matsumuraeses spp., Melanagromyza spp., Melipotes spp., Melissopus spp., Melittia spp., Melolontha spp., Meristis spp., Meritastis spp., Merophyas spp., Mesapamea spp., Mesogona spp., Mesoleuca spp., Metanema spp., Metendothenia spp., Metzneria spp., Micardia spp., Microcorses spp., Microleon spp., Mnesictena spp., Mocis spp., Monima spp., Monochroa spp., Monomorium spp., Monomorium pharaonis, Monopsis spp., Morrisonia spp., Musca spp.,

Mutuuraia spp., Myelois spp., Mythimna spp., Myzus spp., Naranga spp., Nedra spp., Nemapogon spp., Neodiprion spp., Neosphaleroptera spp., Nephelodes spp., Nephotettix spp., Nezara spp., Nilaparvata spp., Niphonympha spp., Nippoptilia spp., Noctua spp., Nola spp., Notocelia spp., Notodonta spp., Nudaurelia spp., Ochropleura spp., Ocnerostoma spp., Oestrus spp., Olethreutes spp., Oligia spp., Olindia spp., Olygonychus spp., Olygonychus gallinae, Oncocnemis spp., Operophtera spp., Ophisma spp., Opogona spp., Oraesia spp., Orniodoros spp., Orgyia spp., Oria spp., Orseolia spp., Orthodes spp., Orthogonia spp., Orthosia spp., Oryzaephilus spp., Oscinella spp., Oscinella frit, Osminia spp., Ostrinia spp., Ostrinia nubilalis, Otiorhynchus spp., Ourapteryx spp., Pachetra spp., Pachysphinx spp., Pagyda spp., Paleacrita spp., Paliga spp., Palthis spp., Pammene spp., Pandemis spp., Panemeria spp., Panolis spp., Panolis flammea, Panonychus spp., Parargyresthia spp., Paradiarsia spp., Paralobesia spp., Paranthrene spp., Parapandemis spp., Parapediasia spp., Parastichtis spp., Parasyndemis spp., Paratoria spp., Pareromeme spp., Pectinophora spp., Pectinophora gossypiella, Pediculus spp., Pegomyia spp., Pegomyia hyoscyami, Pelochrista spp., Pennisetia spp., Penstemonia spp., Pemphigus spp., Peribatodes spp., Peridroma spp., Perileucoptera spp., Periplaneta spp., Perizoma spp., Petrova spp., Pexicopia spp., Phalonia spp., Phalonidia spp., Phaneta spp., Phlyctaenia spp., Phlyctinus spp., Phorbia spp., Phragmatobia spp., Phricanthes spp., Phthorimaea spp., Phthorimaea operculella, Phyllocnistis spp., Phyllocoptruta spp., Phyllocoptruta oleivora, Phyllonorycter spp., Phyllophila spp., Phylloxera spp., Pieris spp., Pieris rapae, Piesma spp., Planococus spp., Planotortrix spp., Platyedra spp., Platynota spp., Platyptilia spp., Platysenta spp., Plodia spp., Plusia spp., Plutella spp., Plutella xylostella, Podosesia spp., Polia spp., Popillia spp., Polymixis spp., Polyphagotarsonemus spp., Polyphagotarsonemus latus, Prays spp., Prionoxystus spp., Probole spp., Proceras spp., Prochoerodes spp., Proeulia spp., Proschistis spp., Proselena spp., Proserpinus spp., Protagrotis spp., Proteoteras spp., Protobathra spp., Protoschinia spp., Pselnophorus spp., Pseudaletia spp., Pseudanthonomus spp., Pseudaternelia spp., Pseudaulacaspis spp., Pseudexentera spp., Pseudococus spp., Pseudohermenias spp., Pseudoplusia spp., Psoroptes spp., Psylla spp., Psylliodes spp., Pterophorus spp., Ptycholoma spp., Pulvinaria spp., Pulvinaria aethiopica, Pyralis spp., Pyrausta spp., Pyrgotis spp., Pyrreferra spp., Pyrrharctia spp., Quadraspidiotus spp., Rancora spp., Raphia spp., Reticultermes spp., Retinia spp., Rhagoletis spp, Rhagoletis pomonella. Rhipicephalus spp., Rhizoglyphus spp., Rhizopertha spp., Rhodnius spp., Rhophalosiphum spp., Rhopobota spp., Rhyacia spp., Rhyacionia spp., Rhynchopacha spp., Rhyzosthenes spp., Rivula spp., Rondotia spp., Rusidrina spp., Rynchaglaea spp., Sabulodes

spp., Sahlbergella spp., Sahlbergella singularis, Saissetia spp., Samia spp., Sannina spp., Sanninoidea spp., Saphoideus spp., Sarcoptes spp., Sathrobrota spp., Scarabeidae, Sceliodes spp., Schinia spp., Schistocerca spp., Schizaphis spp., Schizura spp., Schreckensteinia spp., Sciara spp., Scirpophaga spp., Scirthrips auranti, Scoparia spp., Scopula spp., Scotia spp., Scotinophara spp., Scotogramma spp., Scrobipalpa spp., Scrobipalpopsis spp., Semiothisa spp., Sereda spp., Sesamia spp., Sesia spp., Sicya spp., Sideridis spp., Simyra spp., Sineugraphe spp., Sitochroa spp., Sitobion spp., Sitophilus spp., Sitotroga spp., Solenopsis spp., Smerinthus spp., Sophronia spp., Spaelotis spp., Spargaloma spp., Sparganothis spp., Spatalistis spp., Sperchia spp., Sphecia spp., Sphinx spp., Spilonota spp., Spodoptera spp., Spodoptera littoralis, Stagmatophora spp., Staphylinochrous spp., Stathmopoda spp., Stenodes spp., Sterrha spp., Stomoxys spp., Strophedra spp., Sunira spp., Sutyna spp., Swammerdamia spp., Syllomatia spp., Sympistis spp., Synanthedon spp., Synaxis spp., Syncopacma spp., Syndemis spp., Syngrapha spp., Synthomeida spp., Tabanus spp., Taeniarchis spp., Taeniothrips spp., Tannia spp., Tarsonemus spp., Tegulifera spp., Tehama spp., Teleiodes spp., Telorta spp., Tenebrio spp., Tephrina spp., Teratoglaea spp., Terricula spp., Tethea spp., Tetranychus spp., Thalpophila spp., Thaumetopoea spp., Thiodia spp., Thrips spp., Thrips palmi, Thrips tabaci, Thyridopteryx spp., Thyris spp., Tineola spp., Tipula spp., Tortricidia spp., Tortrix spp., Trachea spp., Trialeurodes spp., Trialeurodes vaporariorum, Triatoma spp., Triaxomera spp., Tribolium spp., Tricodectes spp., Trichoplusia spp., Trichoplusia ni, Trichoptilus spp., Trioza spp., Trioza erytreae, Triphaenia spp., Triphosa spp., Trogoderma spp., Tyria spp., Udea spp., Unaspis spp., Unaspis citri, Utetheisa spp., Valeriodes spp., Vespa spp., Vespamima spp., Vitacea spp., Vitula spp., Witlesia spp., Xanthia spp., Xanthorhoe spp., Xanthotype spp., Xenomicta spp., Xenopsylla spp., Xenopsylla cheopsis, Xestia spp., Xylena spp., Xylomyges spp., Xyrosaris spp., Yponomeuta spp., Ypsolopha spp., Zale spp., Zanclognathus spp., Zeiraphera spp., Zenodoxus spp., Zeuzera spp., Zygaena spp.,

It is also possible to control pests of the class Nematoda using the compounds according to the invention. Such pests include, for example,

root knot nematodes, cyst-forming nematodes and also stem and leaf nematodes; especially of Heterodera spp., e.g. Heterodera schachtii, Heterodora avenae and Heterodora trifolii; Globodera spp., e.g. Globodera rostochiensis; Meloidogyne spp., e.g. Meloidogyne incognita and Meloidogyne javanica; Radopholus spp., e.g. Radopholus similis; Pratylenchus, e.g. Pratylenchus neglectans and Pratylenchus penetrans; Tylen-

chulus, e.g. Tylenchulus semipenetrans; Longidorus, Trichodorus, Xiphinema, Ditylenchus, Apheenchoides and Anguina; especially Meloidogyne, e.g. Meloidogyne incognita, and Heterodera, e.g. Heterodera glycines.

An especially important aspect of the present invention is the use of the compounds of formula (I) according to the invention in the protection of plants against parasitic feeding pests.

The action of the compounds according to the invention and the compositions comprising them against animal pests can be significantly broadened and adapted to the given circumstances by the addition of other insecticides, acaricides or nematicides. Suitable additives include, for example, representatives of the following classes of active ingredient: organophosphorus compounds, nitrophenols and derivatives, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons, neonicotinoids and Bacillus thuringiensis preparations.

Examples of especially suitable mixing partners include: azamethiphos; chlorfenvinphos; cypermethrin, cypermethrin high-cis; cyromazine; diafenthiuron; diazinon; dichlorvos; dicrotophos; dicyclanil; fenoxycarb; fluazuron; furathiocarb; isazofos; iodfenphos; kinoprene; lufenuron; methacriphos; methidathion; monocrotophos; phosphamidon; profenofos; diofenolan; a compound obtainable from the Bacillus thuringiensis strain GC91 or from strain NCTC11821; pymetrozine; bromopropylate; methoprene; disulfoton; quinalphos; taufluvalinate: thiocyclam; thiometon; aldicarb; azinphos-methyl; benfuracarb; bifenthrin; buprofezin; carbofuran; dibutylaminothio; cartap; chlorfluazuron; chlorpyrifos; cyfluthrin; lambda-cyhalothrin; alpha-cypermethrin; zeta-cypermethrin; deltamethrin; diflubenzuron; endosulfan; ethiofencarb; fenitrothion; fenobucarb; fenvalerate; formothion; methiocarb; heptenophos; imidacloprid; thiamethoxam; clothianidin; isoprocarb; methamidophos; methomyl; mevinphos; parathion; parathion-methyl; phosalone; pirimicarb; propoxur; teflubenzuron; terbufos; triazamate; fenobucarb; tebufenozide; fipronil; beta-cyfluthrin; silafluofen; fenpyroximate; pyridaben; fenazaquin; pyriproxyfen; pyrimidifen; nitenpyram; acetamiprid; emamectin; emamectin-benzoate; spinosad; a plant extract that is active against insects; a preparation that comprises nematodes and is active against insects; a preparation obtainable from Bacillus subtilis; a preparation that comprises fungi and is active against insects; a preparation that comprises viruses and is active against insects; chlorfenapyr; acephate; acrinathrin; alanycarb; alphamethrin; amitraz; AZ 60541; azinphos A; azinphos M; azocyclotin; bendiocarb; bensultap; beta-cyfluthrin; BPMC; brofenprox; bromophos A;

bufencarb; butocarboxin; butylpyridaben; cadusafos; carbaryl; carbophenothion; chloethocarb: chlorethoxyfos; chlormephos; cis-resmethrin; clocythrin; clofentezine; cyanophos; cycloprothrin; cyhexatin; demeton M; demeton S; demeton-S-methyl; dichlofenthion; dicliphos; diethion; dimethoate; dimethylvinphos; dioxathion; edifenphos; esfenvalerate; ethion; ethofenprox; ethoprophos; etrimphos; fenamiphos; fenbutatin oxide; fenothiocarb; fenpropathrin; fenpyrad; fenthion; fluazinam; flucycloxuron; flucythrinate; flufenoxuron; flufenprox; fonophos; fosthiazate; fubfenprox; HCH; hexaflumuron; hexythiazox; IKI-220; iprobenfos; isofenphos; isoxathion; ivermectin; malathion; mecarbam; mesulfenphos; metaldehyde; metolcarb; milbemectin; moxidectin; naled; NC 184; omethoate; oxamyl; oxydemethon M; oxydeprofos; permethrin; phenthoate; phorate; phosmet; phoxim; pirimiphos M; pirimiphos E; promecarb; propaphos; prothiofos; prothoate; pyrachlophos; pyradaphenthion; pyresmethrin; pyrethrum; tebufenozide; salithion; sebufos; sulfotep; sulprofos; tebufenpyrad; tebupirimphos; tefluthrin; temephos; terbam; tetrachlorvinphos; thiacloprid: thiafenox; thiodicarb; thiofanox; thionazin; thuringiensin; tralomethrin; triarathene; triazophos; triazuron; trichlorfon; triflumuron; trimethacarb; vamidothion; xylylcarb; Yl 5301/5302; zetamethrin; DPX-MP062 — indoxacarb; methoxyfenozide; bifenazate; XMC (3,5-xylyl methylcarbamate); or the fungus pathogen Metarhizium anisopliae.

The compounds according to the invention can be used to control, i.e. to inhibit or destroy, pests of the mentioned type occurring on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forestry, or on parts of such plants, such as the fruits, blossoms, leaves, stems, tubers or roots, while in some cases plant parts that grow later are still protected against those pests.

Target crops include especially cereals, such as wheat, barley, rye, oats, rice, maize and sorghum; beet, such as sugar beet and fodder beet; fruit, e.g. pomes, stone fruit and soft fruit, such as apples, pears, plums, peaches, almonds, cherries and berries, e.g. strawberries, raspberries and blackberries; leguminous plants, such as beans, lentils, peas and soybeans; oil plants, such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil, cocoa and groundnuts; cucurbitaceae, such as marrows, cucumbers and melons; fibre plants, such as cotton, flax, hemp and jute; citrus fruits, such as cranges, lemons, grapefruit and mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes and paprika; lauraceae, such as avocado, cinnamon and camphor; and tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, vines, hops, bananas, natural rubber plants and ornamentals.

Further areas of use of the compounds according to the invention are the protection of stored goods and storerooms and the protection of raw materials, and also in the hygiene sector, especially the protection of domestic animals and productive livestock against pests of the mentioned type, more especially the protection of domestic animals, especially cats and dogs, from infestation by fleas, ticks and nematodes.

The invention therefore relates also to pesticidal compositions, such as emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, wettable powders, soluble powders, dispersible powders, wettable powders, dusts, granules and encapsulations of polymer substances, that comprise at least one of the compounds according to the invention, the choice of formulation being made in accordance with the intended objectives and the prevailing circumstances.

The active ingredient is used in those compositions in pure form, a solid active ingredient, for example, in a specific particle size, or preferably together with at least one of the adjuvants customary in formulation technology, such as extenders, e.g. solvents or solid carriers, or surface-active compounds (surfactants). In the area of parasite control in humans, domestic animals, productive livestock and pets it will be self-evident that only physiologically tolerable additives are used.

Solvents are, for example: non-hydrogenated or partly hydrogenated aromatic hydrocarbons, preferably fractions C₈ to C₁₂ of alkylbenzenes, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane, alcohols, such as ethanol, propanol or butanol, glycols and ethers and esters thereof, such as propylene glycol, dipropylene glycol ether, ethylene glycol or ethylene glycol monomethyl or -ethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, non-epoxidized or epoxidized plant oils, such as non-epoxidized or epoxidized rapeseed, castor, coconut or soya oil, and silicone oils.

Suitable carriers and adjuvants include all substances customarily used in crop protection products, especially products for the control of slugs and snails.

The solid carriers used, for example for dusts and dispersible powders, are as a rule natural rock powders, such as calcite, talc, kaolin, montmorillonite or attapulgite. Highly disperse silicic acids or highly disperse absorbent polymers can also be added to improve the physical properties. Granular adsorptive granule carriers are porous types, such as pumice, crushed brick, sepiolite or bentonite, and non-sorbent carrier materials are calcite or

sand. A large number of granular materials of inorganic or organic nature can furthermore be used, in particular dolomite or comminuted plant residues.

Surface-active compounds are, depending on the nature of the active compound to be formulated, nonionic, cationic and/or anionic surfactants or surfactant mixtures with good emulsifying, dispersing and wetting properties. The surfactants listed below are to be regarded only as examples; many other surfactants which are customary in formulation technology and are suitable according to the invention are described in the relevant literature.

Nonionic surfactants are, in particular, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols. Substances which are furthermore suitable are water-soluble polyethylene oxide adducts, containing 20 to 250 ethylene glycol ether and 10 to 100 propylene glycol ether groups, on propylene glycol, ethylene diaminopolypropylene glycol and alkyl polypropylene glycol having 1 to 10 carbon atoms in the alkyl chain. The compounds mentioned usually contain 1 to 5 ethylene glycol units per propylene glycol unit. Examples are nonylphenol-polyethoxyethanols, castor oil polyglycol ethers, polypropylene-polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Other substances are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate.

The cationic surfactants are, in particular, quaternary ammonium salts which contain, as substituents, at least one alkyl radical having 8 to 22 C atoms and, as further substituents, lower, non-halogenated or halogenated alkyl, benzyl or lower hydroxyalkyl radicals. The salts are preferably in the form of halides, methyl-sulfates or ethyl-sulfates. Examples are stearyl-trimethyl-ammonium chloride and benzyl-di-(2-chloroethyl)-ethyl-ammonium bromide.

Suitable anionic surfactants can be both water-soluble soaps and water-soluble synthetic surface-active compounds. Suitable soaps are the alkali metal, alkaline earth metal and substituted or unsubstituted ammonium salts of higher fatty acids (C₁₀-C₂₂), such as the sodium or potassium salts of oleic or stearic acid, or of naturally occurring fatty acid mixtures, which can be obtained, for example, from coconut oil or tall oil; and furthermore also the fatty acid methyl-taurine salts. However, synthetic surfactants are more frequently used, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or

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alkylarylsulfonates. The fatty sulfonates and sulfates are as a rule in the form of alkali metal, alkaline earth metal or substituted or unsubstituted ammonium salts and in general have an alkyl radical of 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals; examples are the sodium or calcium salt of ligninsulfonic acid, of dodecylsulfuric acid ester or of a fatty alcohol sulfate mixture prepared from naturally occurring fatty acids. These also include the salts of sulfuric acid esters and sulfonic acids of fatty alcohol-ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and a fatty acid radical having about 8 to 22 C atoms. Alkylarylsulfonates are, for example, the sodium, calcium or triethanolammonium salts of dodecylbenzenesulfonic acid, of dibutylnaphthalenesulfonic acid or of a naphthalenesulfonic acid-formaldehyde condensation product. Corresponding phosphates, such as salts of the phosphoric acid ester of a p-nonylphenol-(4-14)-ethylene oxide adduct or phospholipids, can further also be used.

The compositions as a rule comprise 0.1 to 99 %, in particular 0.1 to 95 %, of active compound and 1 to 99.9 %, in particular 5 to 99.9 %, of - at least - one solid or liquid auxiliary, it being possible as a rule for 0 to 25 %, in particular 0.1 to 20 %, of the composition to be surfactants (% is in each case per cent by weight). While concentrated compositions are more preferred as commercial goods, the end user as a rule uses dilute compositions which comprise considerably lower concentrations of active compound. Preferred compositions are composed, in particular, as follows (% = per cent by weight):

Emulsifiable concentrates:

active ingredient: 1 to 90%, preferably 5 to 20% surfactant: 1 to 30%, preferably 10 to 20% solvent: 5 to 98%, preferably 70 to 85%

Dusts:

active ingredient: 0.1 to 10%, preferably 0.1 to 1%

solid carrier: 99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

active ingredient: 5 to 75%, preferably 10 to 50% water: 94 to 24%, preferably 88 to 30% surfactant: 1 to 40%, preferably 2 to 30%

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Wettable powders:

active ingredient: 0.5 to 90%, preferably 1 to 80% surfactant: 0.5 to 20%, preferably 1 to 15% solid carrier: 5 to 99%, preferably 15 to 98%

Granules:

active ingredient: 0.5 to 30%, preferably 3 to 15% solid carrier: 99.5 to 70%, preferably 97 to 85%

The compositions according to the invention may also comprise further solid or liquid adjuvants, such as stabilisers, e.g. vegetable oils or epoxidised vegetable oils (e.g. epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders and/or tackifiers as well as fertilisers or other active ingredients for obtaining special effects, e.g. acaricides, bactericides, fungicides, nematicides, molluscicides or selective herbicides.

The crop protection products according to the invention are prepared in known manner, in the absence of adjuvants, e.g. by grinding, sieving and/or compressing a solid active ingredient or mixture of active ingredients, for example to a certain particle size, and in the presence of at least one adjuvant, for example by intimately mixing and/or grinding the active ingredient or mixture of active ingredients with the adjuvant(s). The invention relates likewise to those processes for the preparation of the compositions according to the invention and to the use of the compounds of formula (!) in the preparation of those compositions.

The invention relates also to the methods of application of the crop protection products, i.e. the methods of controlling pests of the mentioned type, such as spraying, atomising, dusting, coating, dressing, scattering or pouring, which are selected in accordance with the intended objectives and the prevailing circumstances, and to the use of the compositions for controlling pests of the mentioned type. Typical rates of concentration are from 0.1 to 1000 ppm, preferably from 0.1 to 500 ppm, of active ingredient. The rates of application per hectare are generally from 1 to 2000 g of active ingredient per hectare, especially from 10 to 1000 g/ha, preferably from 20 to 600 g/ha.

A preferred method of application in the area of crop protection is application to the foliage of the plants (foliar application), the frequency and the rate of application being dependent upon the risk of infestation by the pest in question. However, the active ingredient can also penetrate the plants through the roots (systemic action) when the locus of the

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plants is impregnated with a liquid formulation or when the active ingredient is incorporated in solid form into the locus of the plants, for example into the soil, e.g. in granular form (soil application). In the case of paddy rice crops, such granules may be applied in metered amounts to the flooded rice field.

The crop protection products according to the invention are also suitable for protecting plant propagation material, e.g. seed, such as fruits, tubers or grains, or plant cuttings, against animal pests. The propagation material can be treated with the composition before planting: seed, for example, can be dressed before being sown. The active ingredients according to the invention can also be applied to grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example to the seed furrow during sowing.

The compositions according to the invention are also suitable for protecting plant propagation material, including genetically modified propagation material, e.g. seed, such as fruits, tubers or grains, or plant seedlings, against animal pests. The propagation material can be treated with the composition before being planted: seed, for example, can be dressed before being sown. The active ingredients according to the invention can also be applied to grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example to the seed furrow during sowing. The invention relates also to such methods of treating plant propagation material and to the plant propagation material so treated.

The following Examples serve to illustrate the invention. They do not limit the invention. Temperatures are given in degrees Celsius; mixing ratios of solvents are given in parts by volume.

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Preparation Examples:

Example P1): Preparation of N-{(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]propoxy}-phenyl)-[(E)-ethoxyimino]-methyl}-2,2,2-trifluoroacetamide of formula

P1.1) 9 g of 3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-benzonitrile and 1.96 g of hydroxylamine hydrochloride are introduced into 200 ml of ethanol. After the addition of 4.75 ml of triethylamine, stirring is carried out at 80°C for 48 hours. The reaction mixture is concentrated and the residue is taken up in ethyl acetate. After washing with water, the organic phase is concentrated. 4-{3-[2,6-Dichloro-4-(3,3-dichloro-allyloxy)phenoxy]-propoxy}-N-hydroxy-benzamidine having a melting point of 146-148°C is obtained.

P1.2) A solution of 790 mg of 4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]propoxy}-N-hydroxy-benzamidine in 20 ml of dimethylformamide is added dropwise in the course of 15 minutes at 0-5°C to 80 mg of sodium hydride 55 % in 10 ml of dimethylformamide. After 3 hours' stirring at 0-5°C, 256 mg of ethyl iodide are added. After being stirred for 16 hours at room temperature the reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phases and purification over silica gel, 4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-N-ethoxy-benzamidine is obtained.

P1.3) 199 mg of 4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-Nethoxy-benzamidine, 40 mg of triethylamine and 69 mg of trifluoroacetic anhydride are stirred in 4 ml of dichloromethane at room temperature for 24 hours. The reaction mixture is poured into dilute hydrochloric acid and extracted with ethyl acetate. After concentration of the organic phases and purification over silica gel, the title compound is obtained. TH-NMR (CDCl₃) 300MHz: 1.36 (t,3H), 2.29 (m,2H), 4.10-4.35 (m,6H), 4.59 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.95 (d,2H), 7.42 (d,2H), 8.62 (s,1H)

<u>Example P2):</u> Preparation of 6-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-3,4-dihydro-2H-naphthalen-1-one O-methyl-oxime of formula

P2.1) 1.1 g of methanesulfonic acid 3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propyl ester, 1.1 g of potassium carbonate and 0.45 g of 6-hydroxy-1-tetralone are stirred in 10 ml of dimethylformamide at 50°C for 17 hours. The reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phases and purification over silica gel, 6-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-3,4-dihydro-2H-naphthalen-1-one is obtained.

P2.2) 1.24 g of 6-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-3,4-dihydro-2H-naphthalen-1-one, 0.23 g of sodium acetate and 0.23 g of O-methylhydroxyl-amine hydrochloride are stirred in 10 ml of ethanol at 50°C for 18 hours. The reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phases and purification over silica gel, the title compound is obtained. M.p. 75-77°C

<u>Example P3):</u> Preparation of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-2-methoxy-ethanone O-methyl-oxime of formula

P3.1) 3.0 g of 2-bromo-1-(4-hydroxy-phenyl)-ethanone in 25 ml of methanol are added dropwise in the course of 10 minutes to a solution of 7.5 g of sodium methanolate in 80 ml of methanol. Stirring is then carried out at 60°C for 45 minutes. The reaction mixture is cooled, poured into dilute hydrochloric acid and extracted with ethyl acetate. After concentration of the organic phases and crystallisation from diethyl ether, 1-(4-hydroxy-phenyl)-2-methoxy-ethanone is obtained. ¹H-NMR (CDCl₃) 300MHz: 3.50 (s,3H), 4.70 (s,2H), 6.62 (s,1H), 6.91 (d,2H), 7.89 (d,2H)

P3.2) 1.8 g of methanesulfonic acid 3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propyl ester, 1.8 g of potassium carbonate and 1.97 g of 1-(4-hydroxy-phenyl)-2-methoxy-ethanone are stirred in 30 ml of dimethylformamide at 50°C for 17 hours. The reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phases and purification over silica gel, 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-2-methoxy-ethanone is obtained.

P3.3) 296 mg of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-2-methoxy-ethanone, 56 mg of O-methylhydroxylamine hydrochloride and 55 mg of sodium acetate are stirred in 4 ml of methanol at room temperature for 24 hours. The reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phases and purification over silica gel, the title compound is obtained in the form of an E/Z mixture. ¹H-NMR (CDCl₃) 300MHz: 2.30 (m,2H), 3.32+3.46 (s+s,3H), 3.93+3.99 (s+s,3H), 4.18 (t,2H), 4.29 (m,2H), 4.53-4.61 (m,4H), 6.11 (t,1H), 6.83 (s,2H), 6.91 (d,2H), 7.62 (d,2H)

<u>Example P4):</u> Preparation of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-propane-1,2-dione 1-(0-methyl-oxime) of formula

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

P4.1) At 0-2°C, 4.3 g of azodicarboxylic acid diisopropyl ester are added dropwise to 5.6 g of triphenylphosphine in 100 ml of tetrahydrofuran. After 30 minutes' stirring, a solution of 6.7 g of 3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propan-1-ol and 2.9 g of 1-(4-hydroxy-phenyl)-propan-2-one in 100 ml of tetrahydrofuran is added dropwise at 0-2°C in the course of 45 minutes. After 2 hours at from 0 to 2°C and 6 hours at room temperature, the reaction mixture is concentrated and the residue is purified over silica gel. 1-(4-{3-[2,6-Dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-propan-2-one is obtained.

¹H-NMR (CDCl₃) 300MHz: 2.16 (s,3H), 2.30 (m,2H), 3.63 (s,2H), 4.17 (t,2H), 4.27 (t,2H), 4.58 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.90 (d,2H), 7.11 (d,2H)

P4.2) 2.0 g of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-propan-2-one are introduced into 4 ml of HCl 5% in dioxane, then 0.6 g of isopentyl nitrite is added dropwise thereto. After 1 hour's stirring at room temperature, 0.8 ml of triethylamine is

added. The reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phase and purification over silica gel, 1-(4-{3-[2,6-dichloro-4-(3,3dichloro-allyloxy)-phenoxy}-propoxy}-phenyl)-propane-1,2-dione 1-oxime is obtained. ¹H-NMR (CDCl₃) 300MHz: 2.30 (m,2H), 2.51 (s,3H), 4.16 (t,2H), 4.30 (t,2H), 4.58 (d,2H), 6.11 (t,1H), 6.84 (s,2H), 6.98 (d,2H), 7.34 (d,2H), 8.30 (s,1H)

P4.3) 0.8 g of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy}-propoxy}-phenyl)propane-1,2-dione 1-oxime, 0.43 g of potassium carbonate and 0.26 g of methyl iodide are stirred in 10 ml of dimethylformamide at room temperature for 2 hours. The reaction mixture is poured into water and extracted with ethyl acetate. After concentration of the organic phase and purification over silica gel, the title compound is obtained. ¹H-NMR (CDCl₃) 300MHz: 2.30 (m,2H), 2.51 (s,3H), 4.08 (s,3H), 4.15 (t,2H), 4.29 (t,2H), 4.59 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.95 (d,2H), 7.30 (d,2H)

Example P5): Preparation of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]propoxy}-phenyl)-propane-1,2-dione bis-(O-methyl-oxime) of formula

0.23 g of 1-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)propane-1,2-dione 1-(O-methyl-oxime) and 44 mg of O-methylhydroxylamine hydrochloride are stirred in 5 ml of pyridine at 80°C for 2 hours. The reaction mixture is concentrated; the residue is taken up in ethyl acetate and washed with water. After concentration of the organic phase and purification over silica gel, the title compound is obtained. ¹H-NMR (CDCl₃) 300MHz: 2.12 (s,3H), 2.30 (m,2H), 3.88 (s,3H), 3.94 (s,3H), 4.17 (t,2H), 4.29 (t,2H), 4.59 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.91 (d,2H), 7.29 (d,2H)

<u>Example P6):</u> Preparation of (4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-isoxazol-3-yl-methanone O-ethyl-oxime

$$O-N$$
 O
 CI
 CI
 CI
 CI
 CI

P6.1) 40 ml of isopentyl nitrite are slowly added dropwise at 0°C to a solution of 15 g of 4-methoxy-acetophenone and 77 ml of 5.2N HCl in dioxane in 77 ml of diethyl ether and then stirred at room temperature for 18 hours. The reaction mixture is poured into sodium chloride solution and 200 ml of diethyl ether and extracted with diethyl ether. After concentration of the organic phase, 4-methoxyphenylglyoxylhydroxamyl chloride is obtained as a crude product.

P6.2) 16.8 g of sodium hydrogen carbonate are added in portions at 0°C to 27.3 g of that crude product and 38.5 ml of butyl vinyl ether in 200 ml of isopropanol. After 24 hours at room temperature, 200 ml of tert-butyl methyl ether are added and the reaction mixture is filtered. After concentration of the filtrate and purification over silica gel. 5-butoxy-3-(4-methoxybenzoyl)-2-isoxazoline is obtained.

P6.3) 20.4 g of 5-butoxy-3-(4-methoxybenzoyl)-2-isoxazoline and 1.4 g of p-toluene-sulfonic acid in 200 ml of toluene are stirred under reflux for 8 hours. Stirring with 50 ml of sodium hydrogen carbonate solution is then carried out and the aqueous phase is separated off. After concentration of the organic phase and purification over silica gel, 3-(4-methoxy-benzoyl)isoxazole is obtained in the form of colourless crystals, m.p: 71-73°C.

P6.4) 9.2 ml of boron tribromide in 40 ml of dichloromethane are slowly added at -70°C to 13 g of 3-(4-methoxybenzoyl)isoxazole in 200 ml of dichloromethane and stirring is then carried out at room temperature for 3 days. Then, at 0°C, 50 ml of methanol are added dropwise thereto; concentration is carried out and the residue is stirred with 100 ml of 1N hydrochloric acid and 300 ml of ethyl acetate. After concentration of the organic phase and puritication over silica gel, 3-(4-hydroxybenzoyl)isoxazole is obtained in the form of beige crystals, m.p: 125-127°C.

P6.5) 0.93 ml of azodicarboxylic acid diisopropyl ester is added at 0°C to 1.26 g of triphenylphosphine in 30 ml of tetrahydrofuran and stirring is carried out for 30 minutes.

0.76 g of 3-(4-hydroxybenzoyl)isoxazole and 1.38 g of 3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propan-1-ol in 10 ml of tetrahydrofuran are then added dropwise and stirring is carried out at room temperature for 24 hours. After the reaction mixture has been concentrated and purified over silica gel, (4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]propoxy}-phenyl)-isoxazol-3-yl-methanone is obtained in the form of a colourless oil.

P6.6) 486 mg of (4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}phenyl)-isoxazol-3-yl-methanone in 25 ml of pyridine are stirred with 184 mg of O-ethylhydroxylamine hydrochloride at 110°C for 24 hours. The reaction mixture is concentrated and the residue is stirred with tert-butyl methyl ether and 0.5N hydrochloric acid. After concentration of the organic phase and purification over silica gel, the title compound is obtained.

Example P7: Preparation of 3-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]propoxy}-phenyl)-cyclohexanone O-methyl-oxime

P7.1) 100 ml of n-butyllithium 1.6M in hexane are added dropwise at 0°C to a solution of 20 ml of bromoanisole in 600 ml of diethyl ether. After 2 hours, 20.2 ml of 3-ethoxy-2cyclohexenone in 80 ml of diethyl ether are added dropwise. After 3 hours, 100 ml of 3N hydrochloric acid are added dropwise. The organic phase is separated off and concentrated, and the residue is purified over silica gel. 3-(4-Methoxyphenyl)-2-cyclohexen-1-one is obtained in the form of colourless crystals, m.p.: 83-85°C.

P7.2) 1.5 g of 5 % palladium on active carbon are added to 15.15 g of 3-(4-methoxyphenyl)-2-cyclohexen-1-one in 400 ml of methanol and stirring is carried out in a hydrogen atmosphere for 4 hours. The catalyst is filtered off and the reaction mixture is concentrated. The mixture so obtained is dissolved in 200 ml of dichloromethane and stirred with 26.9 g of pyridinium dichromate and 2.1 g of pyridinium trifluoroacetate at room temperature for 6 hours. The reaction mixture is decanted, concentrated and purified over silica gel. 3-(4-Methoxyphenyl)cyclohexanone is obtained in the form of a colourless oil.

P7.3) 2.12 ml of 48% aqueous hydrobromic acid are added slowly to 1.28 g of 3-(4methoxyphenyl)cyclohexanone in 6.4 ml of acetic anhydride. After 4 hours at reflux, the

reaction mixture is poured into ice-water and extracted with diethyl ether. After concentration of the organic phase and purification over silica gel, 3-(4-hydroxyphenyl)cyclohexanone is obtained in the form of an oil.

P7.4) 0.39 ml of azodicarboxylic acid diisopropyl ester is added at 0°C to 0.52 g of triphenylphosphine in 20 ml of tetrahydrofuran. After 30 minutes, 289 mg of 3-(4-hydroxy-phenyl)cyclohexanone and 554 mg of 3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propan-1-ol in 10 ml of tetrahydrofuran are added dropwise thereto. After 24 hours at room temperature, the reaction mixture is concentrated and the residue is purified over silica gel. 3-(4-{3-[2,6-Dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-cyclohexanone is obtained in the form of a colourless oil.

P7.5) 109 mg of 3-(4-{3-[2,6-dichloro-4-(3,3-dichloro-allyloxy)-phenoxy]-propoxy}-phenyl)-cyclohexanone and 21 mg of O-methylhydroxylamine hydrochloride are stirred in 5 ml of pyridine at 85°C for 3 hours. The reaction mixture is concentrated and the residue is stirred with tert-butyl methyl ether and 0.5N hydrochloric acid. After concentration of the organic phase and purification over silica gel, the title compound is obtained in the form of a colourless oil.

Example P8): The compounds listed in the Tables are obtained in the form of E/Z isomeric mixtures, although only one isomer is indicated in column E. In the Tables, m.p. indicates the melting point in °C; n_D^{20} is the refractive index.

Table 1: Compounds of formula

$$E - O - [CH_2]_3 - O - CI$$

is a covalent bond between E and the remainder of the structure

Ño.	E	¹ H-NMR (CDCl₃) 300MHz; m.p. or n _D ²⁰
1.1	O N O O O O O O O O O O O O O O O O O O	1.36 (t,3H), 2.29 (m,2H), 4.10-4.35 (m,6H), 4.59 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.95 (d,2H), 7.42 (d,2H), 8.62 (s,1H)

No.	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.2	,o. _N	2.30 (m,2H), 3.32+3.46(s+s,3H), 3.93+3.99 (s+s,3H), 4.18 (t,2H), 4.29 (m,2H), 4.53-4.61 (m,4H), 6.11 (t,1H), 6.83 (s,2H), 6.91 (d,2H), 7.62 (d,2H)
1.3	O.N.	oil
1.4	~ O N C	oil
1.5	CO.N.C.	oil
1.6	N. O	2.30 (m,2H), 2.51 (s,3H), 4.08 (s,3H), 4.15 (t,2H), 4.29 (t,2H), 4.59 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.95 (d,2H), 7.30 (d,2H)
1.7	N.O.	oil
1.8	-0.N -0	2.12 (s,3H), 2.30 (m,2H), 3.88 (s,3H), 3.94 (s,3H), 4.17 (t,2H), 4.29 (t,2H), 4.59 (d,2H), 6.11 (t,1H), 6.83 (s,2H), 6.91 (d,2H), 7.29 (d,2H)
1.9		oil
1.10	, O.N N.O	oil

No.	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.11	0 N N N N N N	oil
1.12	O-N	oil
1.13	O-N	oil
1.14	O-N	oil
1.15	O-N	oil
1.16	`o-N	m.p. 75-77°C
1.17	O-N	oil
1.18	O-N	oil
1.19	O-N	oil
1.20	O.N.	n _D ²⁰ : 1.5680

	F	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
No.	E	
1.21	.6	n _D ²⁰ : 1.5686
	0.N	
1.22		1.5686
	0	·
	N O	
1.23	Y	n _D ²⁰ : 1.5650
	Ó	
	O.N.	
1.24	Y	n _D ²⁰ : 1.5603
	Ó	
	O.N.	
1.25	Y	n _D ²⁰ : 1.5639
	N . N .	
1.26	N.O	oil
1.27	100	oil
	S. N.	
1.28	0	oil
	s N.O	
1.29	`o.N_	oil
		·

No.	Е	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.30	,0. _N ,0.	oil
1.31	o.N	oil
1.32	O.N.	oil
1.33	ò.N	oil
1.34	O.N.	oil
1.35	O-N	
1.36	O-N	
1.37	s No	oil
1.38	S NO	oil
1.39	O.N.	oil

No.	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.40	N.O	oil
1.41	0-N J	resin
	O-N	
1.42	N.O	resin
1.43	N O	oil
1.44	NO NO	oil
1.45	O.N.	oil
1.46	O.N.	
1.47	O.N	
1.48	-0.N	oil
1.49	~0.N	

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		1 1.1.2 (ODGL) 200MHz: m.p. or n. 20
No.	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.50	0.N	
1.51	O. ₂	
1.52	O.N	
1.53	0.N	oil
1.54	O.N.	
1.55	NO.N.	oil
1.56	0.N	oil
1.57	NO N	oil

		¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
No.	E	n_D^{20} : 1.5510
1.58	O.N CF3	n _D == 1.5510
1.59	N.O.	oil
1.60	,o. _N	oil
1.61	-0.N	oil
1.62	0.N	oil
1.63	~0.N	oil
1.64	0.N	oil

No.	E	¹ H-NMR (CDCl₃) 300MHz; m.p. or n _D ²⁰
1.65	\$-\\	oil
	.0.,	
	O.N.	
1.66	S	oil
	0.N	
1.67		oil
1.07	0. _N	
	Br	
1.68		oil
	Ö. _N	
	Br	
1.69		resin
	O.N	
	Br N	
		resin
1.70	0	Tesiii
	N.N.	
	Br	
1 774		resin
1.71		16311
	Br N N	
	Ĭ	
L		

		11
No.	E	¹ H-NMR (CDCl₃) 300MHz; m.p. or n _D ²⁰
1.72	Br N N	resin
1.73	0-N 0-N	oil
1.74	9. N	oil
1.75	CI N	oil
1.76	CI N	oil
1.77	Br N N	resin
1.78	Br N N	resin

		11
No.	E	¹ H-NMR (CDCl₃) 300MHz; m.p. or n _D ²⁰
1.79	F ₃ C	resin
1.80	F ₃ C	resin
1.81	ON NOTICE OF THE PROPERTY OF T	resin
1.82). _N	resin
1.83	O-N	oil
1.84	-0.N=	oil
1.85	N=CN	oil

No	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
No.		
1.86		
1.87		
1.88		oil .
1.89		
1.90		oil
1.91		oil
1.92	F ₃ C S O	

No.	Е	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.93	F ₃ C S O	
1.94	-O.N S	n _D ²⁰ : 1.5951
1.95	O.N.	n _D ²⁰ : 1.5876
1.96	O.N.	
1.97	S S	
1.98	-0. _N	oil
1.99	-0. _N - S	oil

No.	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.101	NO.N.S.	n _D ²⁰ : 1.5880
1.102	O. _N	
1.103		oil
1.104		m.p. 64-66°C
1.105		oil
1.106	F ₃ C_O	m.p. 96-97°C
1.107		oil
1.10		oil
1.10	9 0=0	oil

No.	E	¹ H-NMR (CDCl ₃) 300MHz; m.p. or n _D ²⁰
1.110		oil
	%-N	
1.111		oil
· <u></u>	Ls	
1.112	N	oil
1.113	N S C	oil
1.114	Br	m.p. 90-94°C
1.115	Br	m.p. 100-108°C
1.116		resin
1.117		m.p. 135-137°C
1.118	S ON N	m.p. 79-81°C

No.	Е	¹ H-NMR (CDCl₃) 300MHz; m.p. or n _D ²⁰
1.119		m.p. 67-69°C

Table A: Compounds of formulae

$ \begin{array}{c} O \\ N \\ N \\ R_5 \end{array} $ $ \begin{array}{c} CI \\ O \\ CI \end{array} $ $ \begin{array}{c} X_1 \\ X_2 \end{array} $	(Ic)
CI CI CI X_2 CI X_2 CI X_2 CI X_2	(ld)
$ \begin{array}{c c} CI & O & X_1 \\ N & O & CI & X_2 \end{array} $ $ \begin{array}{c c} R_5 & CI & O & X_1 \end{array} $	(le)
CI CI CI X_2 X_2 CI X_2 X_2	(If)
$O \xrightarrow{N} O - [CH_2]n - O \xrightarrow{CI} X_2$	(lg)
$\begin{array}{c c} CI & O & X_1 \\ \hline & O & X_2 \\ \hline & R_5 & CI & CI \\ \hline & CI & CI & X_2 \\ \hline & CI & X_3 \\ \hline & CI & X_2 \\ \hline & CI & X_2 \\ \hline & CI & X_3 \\ \hline & CI & X_2 \\ \hline & CI & X_3 \\ \hline & CI & X_3$	(lh)
$\begin{array}{c c} CI & O & X_1 \\ \hline & O & CI & X_2 \end{array}$	(li)

$\begin{array}{c c} Cl & O \\ \hline \\ N \\ R_5 & Cl \\ \hline \end{array}$ $(C=O)NH - [CH_2]n - O Cl \\ Cl & X_2$	(lj)
$\begin{array}{c c} CI & O & X_1 \\ \hline O & R_5 & O - [CH_2]n - O & CI \end{array}$	(lk)
$\begin{array}{c c} CI & O & X_1 \\ \hline & & $	(lm)
$ \begin{array}{c c} CI & O \\ \hline CI & X_1 \\ \hline X_2 & CI \end{array} $ $ \begin{array}{c c} CI & O \\ \hline CI & X_2 \end{array} $	(In)
$ \begin{array}{c} CI \\ O \\ R_6 \end{array} $ $ \begin{array}{c} CI \\ CI \end{array} $ $ \begin{array}{c} X_1 \\ X_2 \end{array} $	(lo)

No.	R ₅
A.1	CH₂OCH₃
A.2	CH ₂ OC ₂ H ₅
A.3	CH ₂ O-n-C ₃ H ₇
A.4	CH₂O-n-C₄H ₉
A.5	CH ₂ O-n-C ₅ H ₁₁
A.6	CH ₂ O-n-C ₆ H ₁₃
A.7	CH₂O-iso-C₃H ₇
A.8	CH₂O-iso-C₄H ₉
A.9	CH ₂ O-iso-C ₅ H ₁₁
A.10	CH₂O-tert-C₄H ₉
A:.11	CH ₂ OCH ₂ C(CH ₃) ₃
A.12	CH₂OCH₂(cyclopropyl)
A.13	CH₂OCF₃
A.14	CH₂OCH₂CF₃
A.15	CH₂OCH₂CHF₂
A.16	CH₂OCH₂CH₂F

R ₅
CH ₂ OCH ₂ CH=CH ₂
CH ₂ OCH ₂ C≡CH
CH ₂ OCH ₂ C≡CCH ₃
CH(CH ₃)-OCH ₃
CH(CH ₃)-OC ₂ H ₅
CH(CH ₃)-O-n-C ₃ H ₇
CH(CH ₃)-O-n-C₄H ₉
CH(CH₃)-O-n-C₅H₁₁
CH(CH ₃)-O-n-C ₆ H ₁₃
CH(CH₃)-O-iso-C₃H ₇
CH(CH ₃)-O-iso-C ₄ H ₉
CH(CH₃)-O-iso-C₅H₁₁
CH(CH₃)-O-tert-C₄H₀
CH(CH ₃)-OCH ₂ C(CH ₃) ₃
CH(CH₃)-OCH₂(cyclopropyl)
CH(CH ₃)-OCF ₃
CH(CH ₃)-OCH ₂ CF ₃
CH(CH ₃)-OCH ₂ CHF ₂
CH(CH ₃)-OCH ₂ CH ₂ F
CH(CH ₃)-OCH ₂ CH=CH ₂
CH(CH ₃)-OCH ₂ C≡CH
CH(CH ₃)-OCH ₂ C≡CCH ₃
C(CH ₃) ₂ -OCH ₃
$C(CH_3)_2$ - OC_2H_5
$C(CH_3)_2$ -O-n- C_3H_7
C(CH ₃) ₂ -O-n-C ₄ H ₉
C(CH ₃) ₂ -O-n-C ₅ H ₁₁
C(CH ₃) ₂ -O-n-C ₆ H ₁₃
$C(CH_3)_2$ -O-iso- C_3H_7
$C(CH_3)_2$ -O-iso- C_4H_9
C(CH ₃) ₂ -O-iso-C ₅ H ₁₁
C(CH ₃) ₂ -O-tert-C ₄ H ₉
C(CH ₃) ₂ -OCH ₂ C(CH ₃) ₃
C(CH ₃) ₂ -OCH ₂ (cyclopropyl)
C(CH ₃) _Z -OCF ₃
C(CH ₃) ₂ -OCH ₂ CF ₃
C(CH ₃) ₂ -OCH ₂ CHF ₂

No.	R ₅
A.54	C(CH ₃) ₂ -OCH ₂ CH ₂ F
A.55	C(CH ₃) ₂ -OCH ₂ CH=CH ₂
A.56	$C(CH_3)_2$ - $OCH_2C\equiv CH$
A.57	C(CH ₃) ₂ -OCH ₂ C≡CCH ₃
A.58	$C(=O)CH_3$
A.59	$C(=O)C_2H_5$
A.60	$C(=O)-n-C_3H_7$
A.61	$C(=O)-\dot{n}-C_4H_9$
A.62	$C(=O)-n-C_5H_{11}$
A.63	$C(=O)-n-C_6H_{13}$
A.64	$C(=O)$ -iso- C_3H_7
A.65	$C(=O)$ -iso- C_4H_9
A.66	$C(=O)$ -iso- C_5H_{11}
A.67	C(=O)-tert-C ₄ H ₉
A.68	C(=O)-cyclopropyl
A.69	C(=N-OCH ₃)CH ₃
A.70	C(=N-OCH ₃)C ₂ H ₅
A.71	C(=N-OCH ₃)-n-C ₃ H ₇
A.72	C(=N-OCH ₃)-n-C ₄ H ₉
A.73	C(=N-OCH ₃)-n-C ₅ H ₁₁
A.74	C(=N-OCH ₃)-n-C ₆ H ₁₃
A.75	C(=N-OCH ₃)-iso-C ₃ H ₇
A.76	C(=N-OCH ₃)-iso-C ₄ H ₉
A.77	C(=N-OCH ₃)-iso-C ₅ H ₁₁
A.78	C(=N-OCH ₃)-tert-C ₄ H ₉
A.79	C(=N-OCH ₃)-cyclopropyl
A.80	C(=N-OCH ₂ CH ₃)CH ₃
A.81	C(=N-OCH ₂ CH ₃)C ₂ H ₅
A.82	C(=N-OCH ₂ CH ₃)-n-C ₃ H ₇
A.83	C(=N-OCH ₂ CH ₃)-n-C ₄ H ₉
A.84	C(=N-OCH ₂ CH ₃)-n-C ₅ H ₁₁
A.85	C(=N-OCH ₂ CH ₃)-n-C ₆ H ₁₃
A.86	C(=N-OCH ₂ CH ₃)-iso-C ₃ H ₇
A.87	C(=N-OCH ₂ CH ₃)-iso-C ₄ H ₉
A.88	C(=N-OCH ₂ CH ₃)-iso-C ₅ H ₁₁
A.89	C(=N-OCH ₂ CH ₃)-tert-C ₄ H ₉
A.90	C(=N-OCH₂CH₃)-cyclopropyl

No.	R ₅
A.91	C(=N-OCH₂CH=CH₂)CH₃
A.92	C(=N-OCH ₂ CH=CH ₂)C ₂ H ₅
A.93	C(=N-OCH ₂ CH=CH ₂)-n-C ₃ H ₇
A.94	C(=N-OCH ₂ CH=CH ₂)-n-C ₄ H ₉
A.95	C(=N-OCH ₂ CH=CH ₂)-n-C ₅ H ₁₁
A.96	C(=N-OCH ₂ CH=CH ₂)-n-C ₆ H ₁₃
A.97	C(=N-OCH ₂ CH=CH ₂)-iso-C ₃ H ₇
A.98	$C(=N-OCH_2CH=CH_2)$ -iso- C_4H_9
A.99	$C(=N-OCH_2CH=CH_2)$ -iso- C_5H_{11}
A.100	C(=N-OCH ₂ CH=CH ₂)-tert-C ₄ H ₉
A.101	C(=N-OCH ₂ CH=CH ₂)-cyclopropyl
A.102	C(=N-OCH ₂ C≡CH)CH ₃
A.103	C(=N-OCH ₂ C≡CH)C ₂ H ₅
A.104	C(=N-OCH ₂ C≡CH)-n-C ₃ H ₇
A.105	C(=N-OCH ₂ C≡CH)-n-C ₄ H ₉
A.106	C(=N-OCH ₂ C=CH)-n-C ₅ H ₁₁
A.107	$C(=N-OCH_2C=CH)-n-C_6H_{13}$
A.108	C(=N-OCH ₂ C=CH)-iso-C ₃ H ₇
A.109	C(=N-OCH ₂ C≡CH)-iso-C ₄ H ₉
A.110	$C(=N-OCH_2C\equiv CH)$ -iso- C_5H_{11}
A.111	C(=N-OCH ₂ C≡CH)-tert-C ₄ H ₉
A.112	C(=N-OCH ₂ C≡CH)-cyclopropyl
A.113	CONHCH₃
A.114	CONHC ₂ H ₅
A.115	CONH-n-C₃H ₇
A.116	CONH-n-C₄H ₉
A.117	CONH-n-C₅H ₁₁
A.118	CONH-n-C ₆ H ₁₃
A.119	CONH-iso-C ₃ H ₇
A.120	CONH-iso-C ₄ H ₉
A.121	CONH-iso-C₅H ₁₁
A.122	CONH-tert-C₄H ₉
A.123	2-thienyl
A.124	3-thienyl
A.125	2-benzo[b]thienyl
A.126	2-benzo[b]furyl

No.	R ₆
A.127	3-isoxazolyl
A.128	4-methyl-3-isoxazolyl
A.129	2-pyridyl
A.130	3-pyridyl
A.131	4-pyridyl
A.132	2-thiazolyl
A.133	2-furyl
A.134	5-bromo-2-thienyl
A.135	5-bromo-2-pyridyl
A.136	6-bromo-3-pyridyl
A.137	5-trifluoromethyl-2-pyridyl
A.138	CH ₂ N(CH ₃)-S(O) ₂ -CH ₃
A.139	CH ₂ N(CH ₃)-S(O) ₂ -CH ₂ CH ₃
A.140	CH₂N(CH₂CH₃)-S(O)₂-CH₃
A.141	CH ₂ N(CH ₂ CH ₃)-S(O) ₂ - CH ₂ CH ₃
A.142	CH ₂ N(CH ₃)-S(O) ₂ -CF ₃
A.143	CH ₂ N(CH ₂ CH ₃)-S(O) ₂ -CF ₃
A.144	5-methoxy-2-pyridyl
A.145	6-methoxy-3-pyridyl

<u>Table 2:</u> A compound of general formula (Ic) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 3:</u> A compound of general formula (Ic) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 4:</u> A compound of general formula (Ic) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 5:</u> A compound of general formula (Ic) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

- <u>Table 6:</u> A compound of general formula (Ic) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 7: A compound of general formula (Ic) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 8:</u> A compound of general formula (If) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 9:</u> A compound of general formula (If) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 10:</u> A compound of general formula (If) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 11:</u> A compound of general formula (If) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 12:</u> A compound of general formula (If) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 13:</u> A compound of general formula (If) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 14:</u> A compound of general formula (le) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 15:</u> A compound of general formula (le) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

- <u>Table 16:</u> A compound of general formula (le) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 17:</u> A compound of general formula (le) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 18:</u> A compound of general formula (Ie) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 19:</u> A compound of general formula (le) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of **Table A.**
- <u>Table 20:</u> A compound of general formula (If) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 21:</u> A compound of general formula (If) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 22:</u> A compound of general formula (If) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 23:</u> A compound of general formula (If) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 24:</u> A compound of general formula (If) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

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<u>Table 25:</u> A compound of general formula (If) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

- <u>Table 26:</u> A compound of general formula (Ig) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 27:</u> A compound of general formula (Ig) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 28:</u> A compound of general formula (Ig) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 29:</u> A compound of general formula (Ig) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of **Table A.**
- <u>Table 30:</u> A compound of general formula (Ig) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 31:</u> A compound of general formula (Ig) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 32:</u> A compound of general formula (Ih) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 33:</u> A compound of general formula (Ih) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 34:</u> A compound of general formula (Ih) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 35:</u> A compound of general formula (Ih) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

- Table 36: A compound of general formula (Ih) wherein X₁ and X₂ are bromine and n is 3, and the substituent R_{5} for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 37: A compound of general formula (Ih) wherein X₁ and X₂ are bromine and n is 5, and the substituent $R_{\scriptscriptstyle 5}$ for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 38: A compound of general formula (Ii) wherein X₁ and X₂ are chlorine and n is 2, and the substituent R_{5} for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 39: A compound of general formula (li) wherein X₁ and X₂ are chlorine and n is 3, and the substituent $R_{\scriptscriptstyle 5}$ for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 40: A compound of general formula (li) wherein X₁ and X₂ are chlorine and n is 5, and the substituent R_{5} for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 41: A compound of general formula (Ii) wherein X₁ and X₂ are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 42: A compound of general formula (Ii) wherein X₁ and X₂ are bromine and n is 3, and the substituent R_{5} for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 43: A compound of general formula (Ii) wherein X₁ and X₂ are bromine and n is 5, and the substituent $R_{\rm 5}$ for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 44: A compound of general formula (Ik) wherein X₁ and X₂ are chlorine and n is 2, and the substituent $R_{\scriptscriptstyle 5}$ for each compound corresponds to a line A.1 to A.145 of Table A.
- Table 45: A compound of general formula (lk) wherein X1 and X2 are chlorine and n is 3, and the substituent R_{δ} for each compound corresponds to a line A.1 to A.145 of Table A.

- <u>Table 46:</u> A compound of general formula (lk) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 47:</u> A compound of general formula (lk) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 48:</u> A compound of general formula (lk) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 49:</u> A compound of general formula (lk) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 50:</u> A compound of general formula (Im) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 51:</u> A compound of general formula (Im) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 52:</u> A compound of general formula (Im) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 53:</u> A compound of general formula (Im) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 54:</u> A compound of general formula (Im) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 55:</u> A compound of general formula (Im) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

- <u>Table 56:</u> A compound of general formula (In) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 57:</u> A compound of general formula (In) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 58:</u> A compound of general formula (In) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 59:</u> A compound of general formula (In) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 60:</u> A compound of general formula (In) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 61:</u> A compound of general formula (In) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 62:</u> A compound of general formula (Io) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 63:</u> A compound of general formula (Io) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 64:</u> A compound of general formula (Io) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 65:</u> A compound of general formula (Io) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

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- <u>Table 66:</u> A compound of general formula (Io) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 67:</u> A compound of general formula (Io) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 68:</u> A compound of general formula (Id) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 69:</u> A compound of general formula (Id) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of **Table A.**
- <u>Table 70:</u> A compound of general formula (Id) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 71:</u> A compound of general formula (Id) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 72:</u> A compound of general formula (Id) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 73:</u> A compound of general formula (Id) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 74:</u> A compound of general formula (Ig) wherein X_1 and X_2 are chlorine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.
- <u>Table 75:</u> A compound of general formula (Ig) wherein X_1 and X_2 are chlorine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 76:</u> A compound of general formula (Ig) wherein X_1 and X_2 are chlorine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 77:</u> A compound of general formula (Ig) wherein X_1 and X_2 are bromine and n is 2, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 78:</u> A compound of general formula (Ig) wherein X_1 and X_2 are bromine and n is 3, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of Table A.

<u>Table 79:</u> A compound of general formula (Ig) wherein X_1 and X_2 are bromine and n is 5, and the substituent R_5 for each compound corresponds to a line A.1 to A.145 of **Table A.**

Formulation Examples (% = percent by weight)

Example F1: Emulsifiable concentrates	a)	b)	c)
active ingredient	25 %	40 %	50 %
calcium dodecylbenzenesulfonate	5 %	8 %	6 %
castor oil polyethylene glycol ether (36 mol EO)	5 %	-	-
tributylphenol polyethylene glycol ether (30 mol EO)	-	12 %	4 %
cyclohexanone	-	15 %	20 %
xylene mixture	65 %	25 %	20 %
Aylene mixtare			

Mixing finely ground active ingredient and additives gives an emulsifiable concentrate which yields emulsions of the desired concentration on dilution with water.

Example F2: Solutions	a) 80 %	b) 10 %	c) 5 %	d) 95 %
active ingredient	80 %	10 /6	5 70	00 70
ethylene glycol monomethyl ether	20 %	-	-	-
polyethylene glycol (MW 400)	-	70 %	-	-
N-methylpyrrolid-2-one	-	20 %	-	-
epoxidised coconut oil	_	-	1 %	5 %
benzine (boiling range: 160-190°)	-	-	94 %	-

Mixing finely ground active ingredient and additives gives a solution suitable for use in the form of microdrops.

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Example F3: Granules	a)	b)	c)	d)
active ingredient	5 %	10 %	8 %	21 %
kaolin	94 %	-	79 %	54 %
highly dispersed silicic acid	1 %	-	13 %	7 %
attapulgite	-	90 %	-	18 %

The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier mixture and the solvent is evaporated off *in vacuo*.

Biological Examples

Example B1: Action against Heliothis virescens caterpillars

Young soybean plants are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of test compound. After the spray-coating has dried, the soybean plants are populated with 10 caterpillars of Heliothis virescens in the first stage and placed in a plastics container. Evaluation is made 6 days later. The percentage reduction in population and the percentage reduction in feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on the untreated plants.

The compounds of formula I exhibit good activity against Heliothis virescens in this test. In particular, the compounds 1.2 to 1.45, 1.48, 1.53, 1.55 to 1.61, 1.63, 1.67 to 1.85, 1.88, 1.90 to 1.91, 1.94 to 1.95, 1.98 to 1.101 and 1.104 to 1.116 are more than 80 % effective.

Example B2: Action against Plutella xylostella caterpillars

Young cabbage plants are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of test compound. After the spray-coating has dried, the cabbage plants are populated with 10 caterpillars of Plutella xylostella in the third stage and placed in a plastics container. Evaluation is made 3 days later. The percentage reduction in population and the percentage reduction in feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on the untreated plants.

The compounds of formula I exhibit good activity against Plutella xylostella in this test. In particular, the compounds 1.2 to 1.45, 1.48, 1.53, 1.55 to 1.61, 1.63, 1.67 to 1.85, 1.88, 1.90 to 1.91, 1.94 to 1.95, 1.98 to 1.101 and 1.104 to 1.116 are more than 80 % effective.

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Example B3: Action against Spodoptera littoralis

Young soybean plants are sprayed with an aqueous emulsion spray mixture comprising 400 ppm of test compound and, after the spray-coating has dried, the plants are populated with 10 caterpillars of Spodoptera littoralis in the first stage and then placed in a plastics container. 3 days later, the percentage reduction in population and the percentage reduction in feeding damage (% activity) are determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

The compounds of formula I exhibit good activity against Spodoptera littoralis in this test. In particular, the compounds 1.2 to 1.45, 1.48, 1.53, 1.55 to 1.61, 1.63, 1.67 to 1.85, 1.88, 1.90 to 1.91, 1.94 to 1.95, 1.98 to 1.101 and 1.104 to 1.116 are more than 80 % effective are more than 80 % effective.